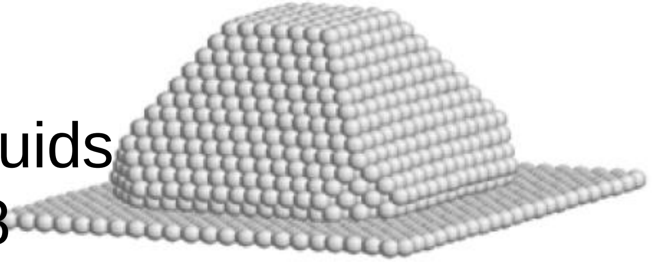
NTNU
Norwegian University of Science and Technology

TMT4320 Nanomaterials
Septemeber 12th, 2016

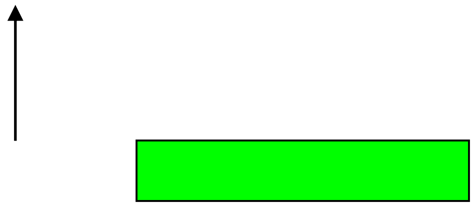
- Synthesis of nanomaterials
  - TNN3. Top-down approach
  - Bottom-up approach
    - Cushing et al. Supercritical fluids
    - NN (Bréchignac). Chapter 18



Last lecture

- Synthesis of nanomaterials
  - Bottom-up approach
    - Hydrothermal/Solvothermal: Supercritical fluids
    - Invited guess: Antoine Dalod
  - Top-down approach
    - High energy ball milling

”Top-down”



”Bottom-up”

Synthesis-Learning objectives

- Different routes for the synthesis of nanoparticles and nanocrystalline materials
  - Bottom-up approach
  - Top-down approach
- Different routes for the consolidation of nanoparticles and nanocrystalline materials

Synthesis of nanomaterials

- Top-down approach
  - A microcrystalline material is fragmented to yield a nanocrystalline material. Ex. Solid state routes.
  - Produce bulk nanostructured materials
  - Be easily scaled up

- Bottom-up approach
  - Individual atoms and molecules are brought together or self-assembled to form nanostructured materials in at least one dimension.
  - Fine nanostructures of individual nanoparticles with narrow size distributions
  - Difficult to scale up

Synthesis of nanomaterials

– Bottom-up approach

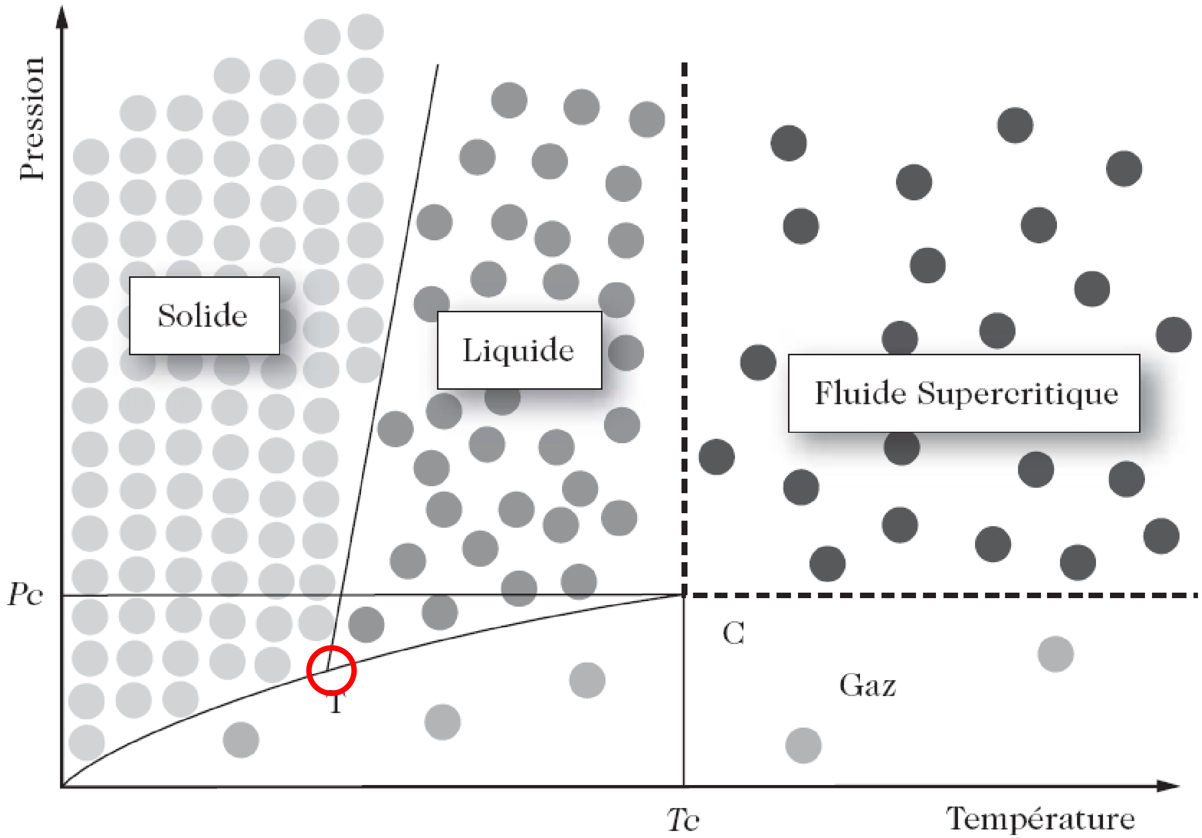
- Supercritical fluids: Hydrothermal/Solvothermal
- Chemical methods
  - Colloidal methods (today)
  - Sol-gel methods
- Vapor phase methods (Maria)
- Consolidation of Nanopowders (sintering)

Supercritical fluid

- Intermediate state between liquid and gas
- Critical point
  - End point of the liquid-vapour coexistence curve in a phase diagram
  - Beyond the fluid is both liquid and gas at the same time, i.e., as dense as the liquid while conserving certain properties of the gas
- Temperature/pressure beyond the critical point

- Phase diagram (S, L, G)
  - Triple point
  - Critical point
  - Changes in density

Supercritical fluid (SF)



Pressure vs. temperature phase diagram of a pure substance. T=triple point, C=critical point.

SCF illustration

Physiochemical properties of SF

- Density
- Solubility
- Viscosity
- Diffusion

Solubility

- What determines the ability of a fluid to solubilize a given substance?
- Dissolving power
  - Depends on the physical and chemical state of the fluid

$$\delta_{\mathrm{f}} = 1.25 P_{\mathrm{c}}^{1/2} \frac{\rho(T, P)}{\rho_{\mathrm{liq}}}$$

  - where P_c is the pressure of the supercritical fluid, ρ is the density of the fluid in g/ml, and ρ_{liq} is the density of the fluid in the standard liquid state, also in g/ml

Viscosity

- Resistance of fluids to flow
- Reflects the extent to which the molecule is able to move around in an environment containing other molecules
- Supercritical fluid: in the range 10^{-4} to 10^{-3} Pa·s
  - Higher than the value for gases
  - 10 to 100 times lower than the value for liquids
  - The coefficient of diffusion of a solute is higher in a supercritical fluid than in a liquid

Diffusion

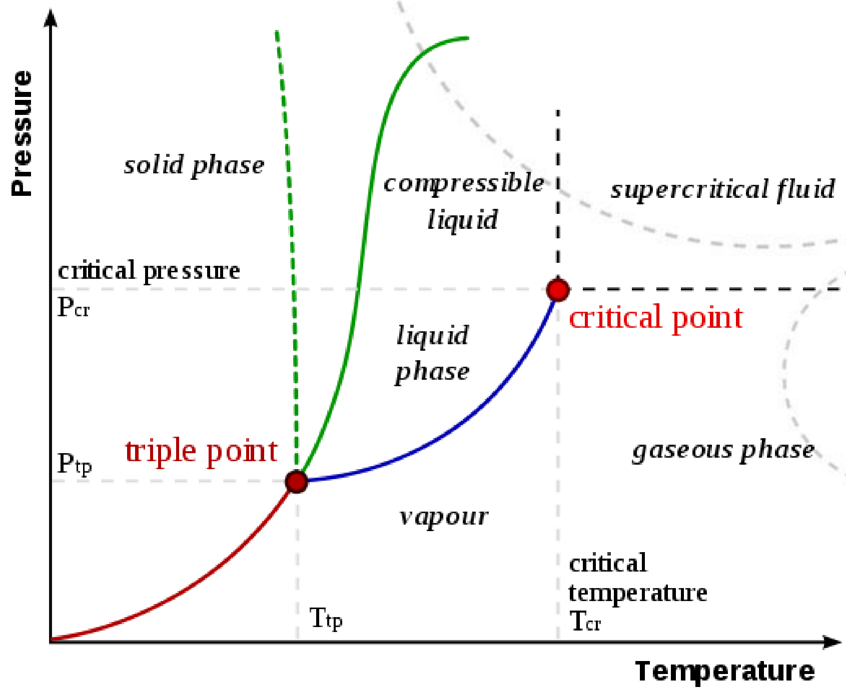
- Higher diffusion in supercritical fluid than in "normal" fluid

Table 20.3. Orders of magnitude of diffusion coefficients in supercritical fluids

	Gas	Supercritical fluid	Liquid
Diffusion coefficient D [$cm^2 s^{-1}$]	$1\text{–}4 \times 10^{-1}$	$10^{-4}\text{–}10^{-3}$	$0.2\text{–}2 \times 10^{-5}$

Hydrothermal synthesis

- A product is crystallized in aqueous environment at temperatures above 100 °C and at pressures from 1-200 bar, approaching the supercritical fluid stage.
- Advantages
  - Increased solubility with temperature and pressure.
  - Enables synthesis of materials that are unstable at higher temperatures.
  - Can control phase, particle shape and particle size.

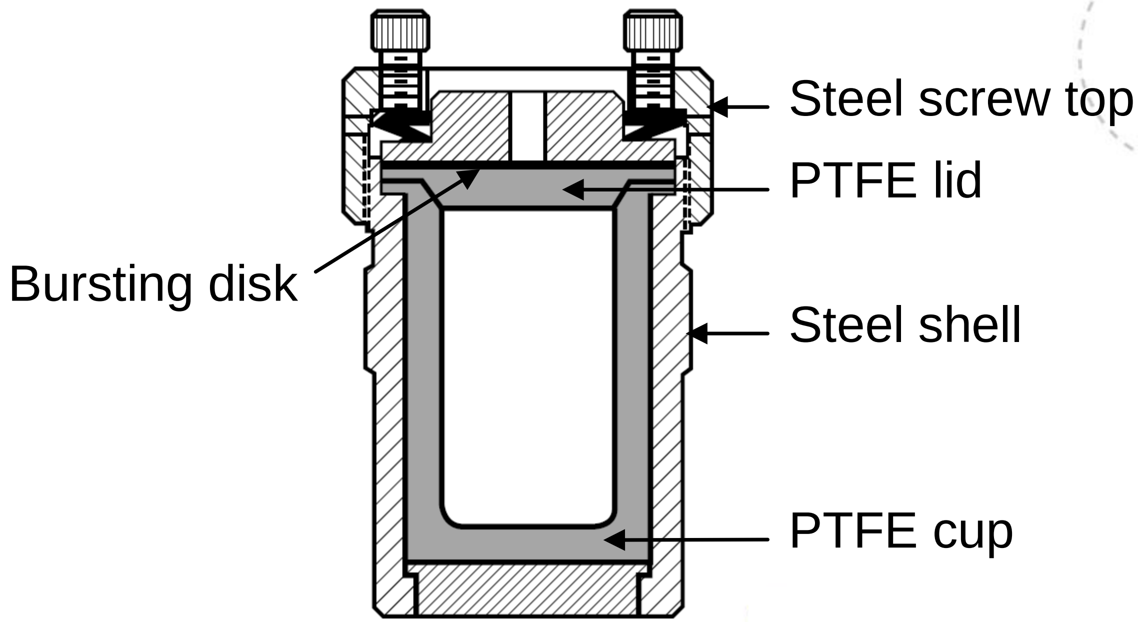


Other solvents than water → solvothermal synthesis

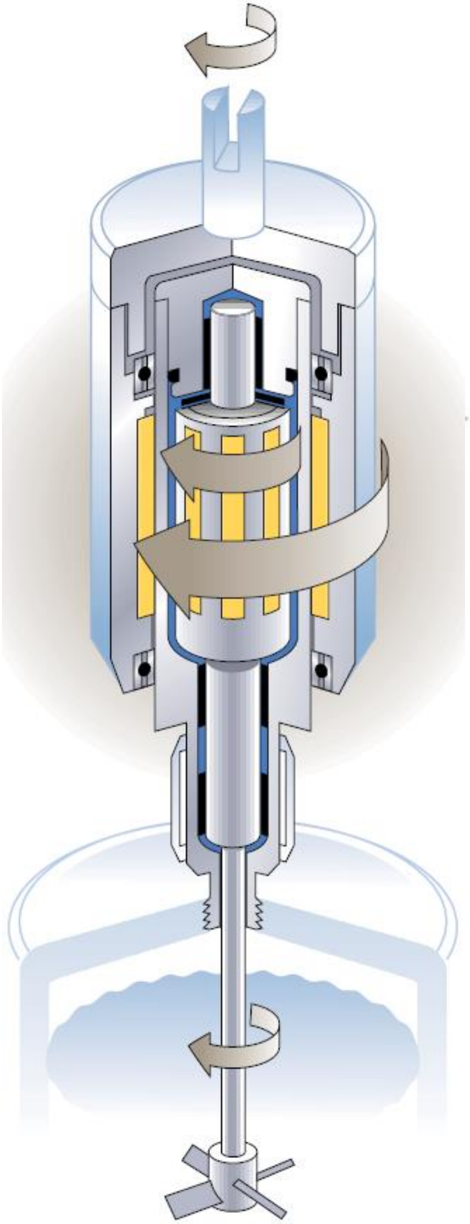
Advantages and disadvantages

- ☺ Temperatures are substantially lower than those required for traditional solid-state reactions
- ☺ Products of solvothermal reactions are usually crystalline and do not require post-annealing treatments
- ☺ Many types of materials can be made
- ☹ Safety issues
  - High pressures
  - Don’t open hot reaction vessels!

Autoclaves

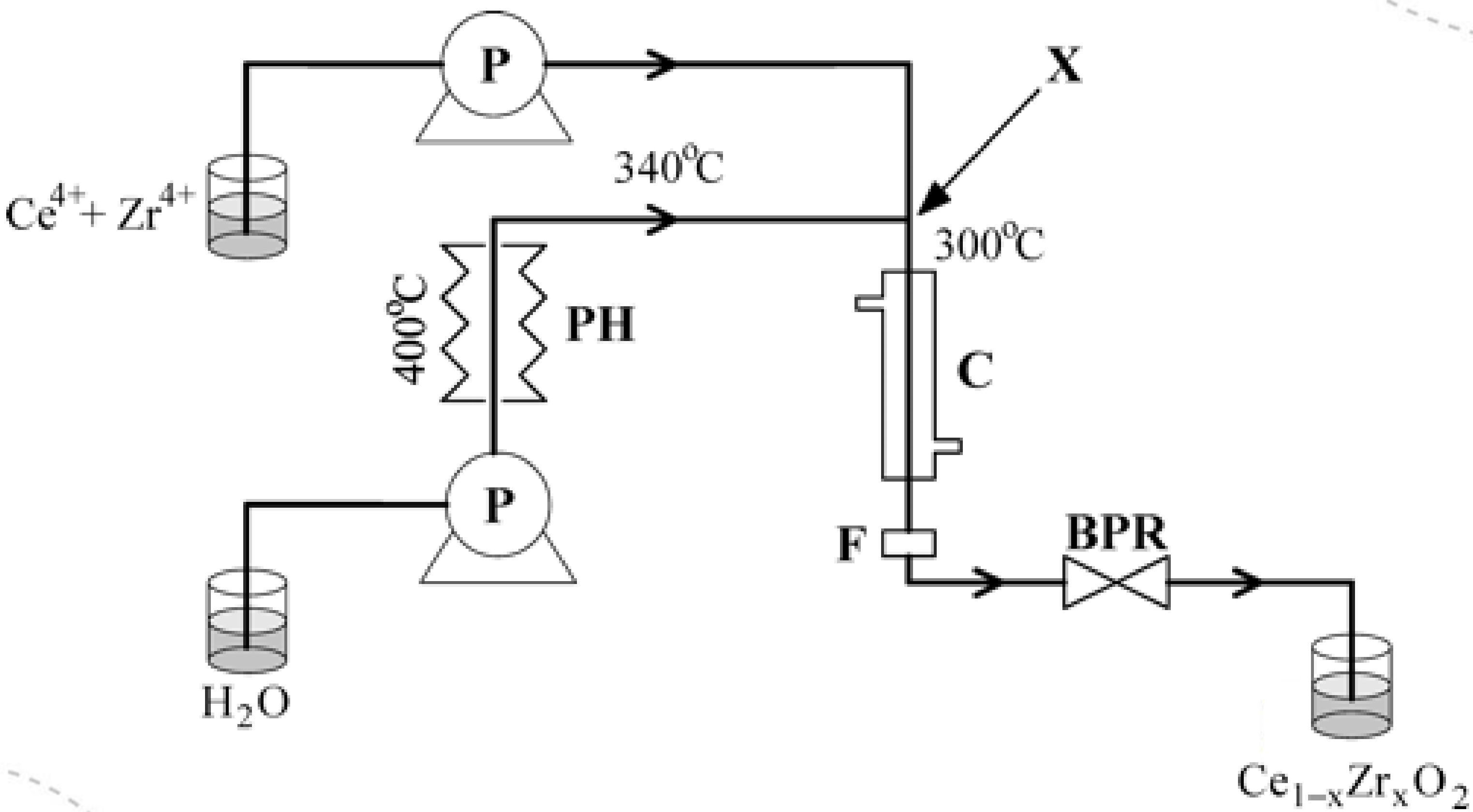


Autoclave with stirring



Continuous-flow hydrothermal reactor

- Particularly relevant given their suitability to large-scale production



NTNU equipment

- NTNU NanoLab
  - 3 × 125 mL autoclaves (Tmax = 250 °C, Pmax = 1900 psi)
  - 2 x 45 mL autoclaves (Tmax = 250 °C, Pmax = 1800 psi)
  - 2 x 23 mL autoclaves (Tmax = 275 °C, Pmax = 5000 psi)
  - 1 autoclave with stirring bar (Tmax = 350 °C, Pmax = 3000 psi)
- Inorganic Materials and Ceramics Research Group
  - 3 × 125 mL autoclaves
  - 3 × 50 mL autoclaves

NTNU research

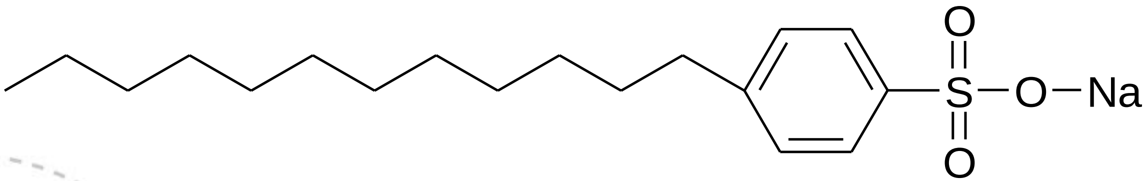
- $PbTiO_3$ nanorods and microspheres
- $KNbO_3$ nanorods
- CeO_2 clusters
- CeO_2@Ca-ZrO_2 core-shell nanospheres
- $CuGaS_2$ powder and thin films
- Zeolites

$PbTiO_3$ nanorods

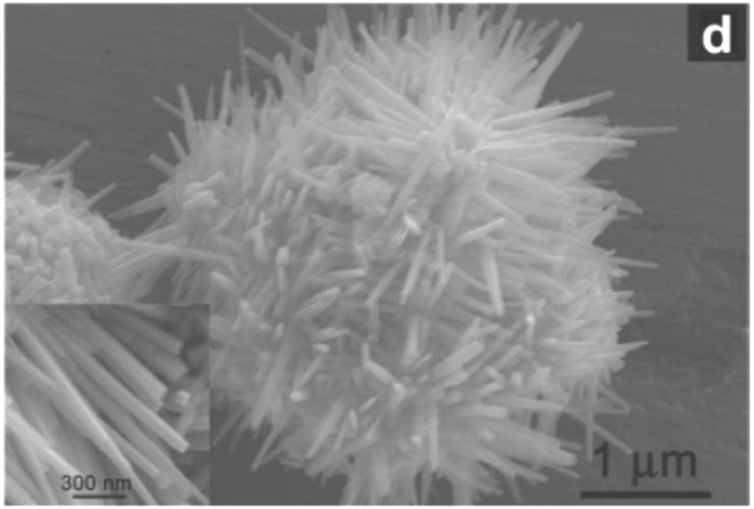
Amorphous $PbTiO_{3-x}(OH)_{2x}$
SDBS surfactant
KOH solution
$SrTiO_3$ substrate

Autoclave
180 °C, 0-48 h, ~14 bar

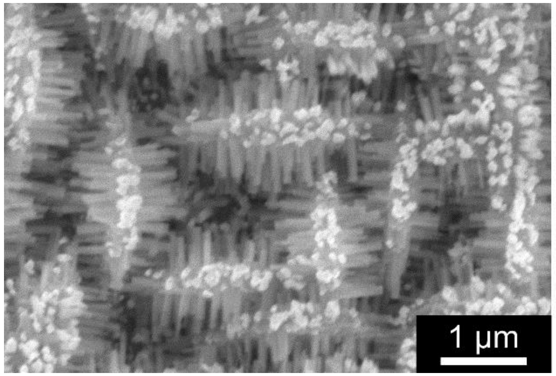
$PbTiO_3$
nanostructures



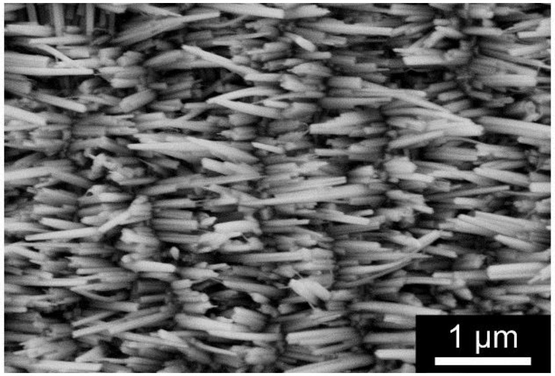
- $PbTiO_3$ bur-like microspheres



- $PbTiO_3$ nanorods on $SrTiO_3$ substrates



(100) $SrTiO_3$ substrate



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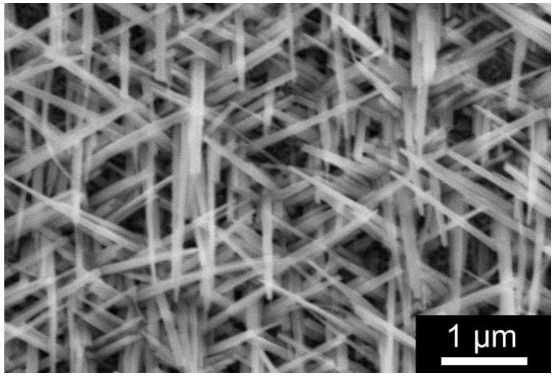
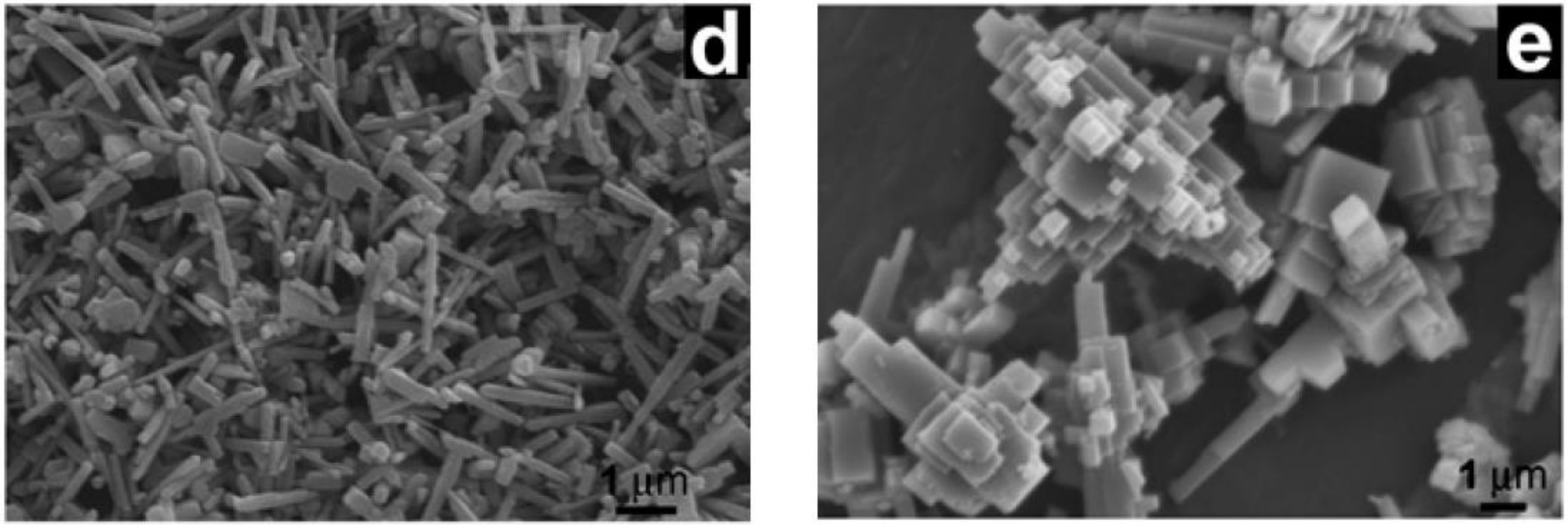


(111)

G. Wang *et al.*, *J. Nanosci. Nanotechnol.*, 2007
G. Wang *et al.*, *Chem. Mater.*, 2007
P. M. Rørvik *et al.*, *Nanotechnology*, 2008
P. M. Rørvik *et al.*, *Cryst. Growth Des.*, 2009

$KNbO_3$ nanorods

- Nb_2O_5, KOH, sodium dodecyl sulfate, water
- 125 mL autoclave
- 180 °C, 48 h

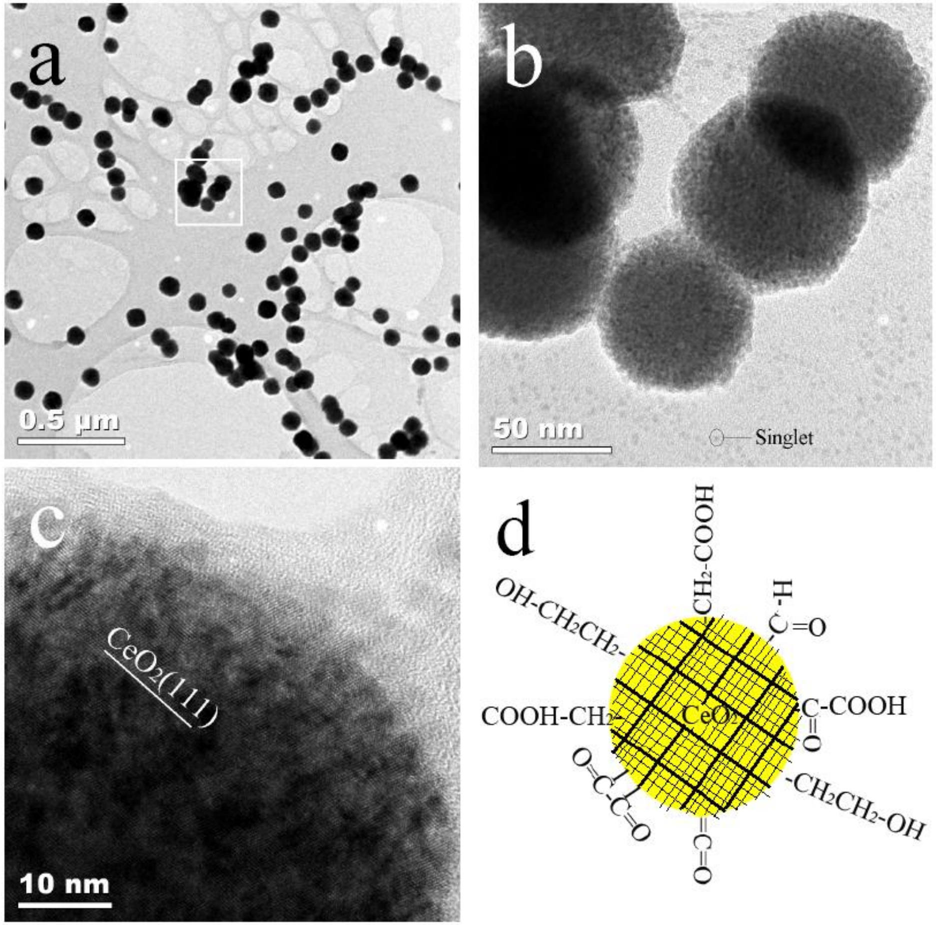


SEM images of $KNbO_3$ products prepared by hydrothermal synthesis at 180 °C for 48 h with increasing amount of SDS: (d) 0.005, (e) 0.01 mol.

G. Wang *et al.*, *Cryst. Eng. Comm.*, 2009

Monodisperse CeO_2 nanoclusters

- $Ce(NO_3)_3$, H_2O_2, ethylene glycol
- 180 °C, 8 h

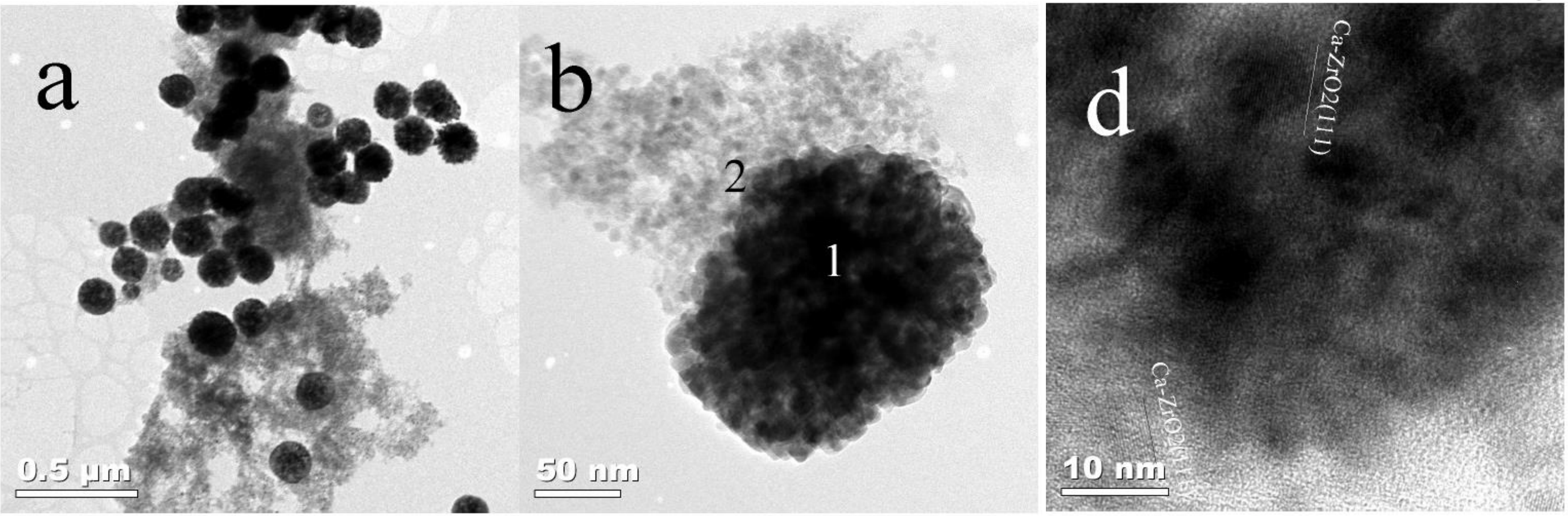


(a)-(c) TEM images of the CeO_2 nanoclusters. (c) HRTEM image. (d) A sketch of the surface modified CeO_2 nanocluster.

Haitao Zhou, Department of Materials Science and Engineering, NTNU, 2009

CeO_2@CSZ core-shell nanospheres

- CSZ = Ca-stabilized ZrO_2 (shell)
- Second hydrothermal step after treatment with $ZrO(NO_3)_3$ and $Ca(NO_3)_2$



TEM images of the CeO_2@CSZ nanoclusters. The HRTEM image in (C) shows the distances between the adjacent two parallel planes are 2.92 nm, which is the $Zr_{0.85}Ca_{0.15}O_{1.85}$ (111) plane.

Haitao Zhou, Department of Materials Science and Engineering, NTNU, 2009

Invited guess: Antoine Dalod

- Hydrothermal synthesis of surface functionalized TiO_2 nanoparticles

Synthesis of nanomaterials

- Top-down approach
  - A microcrystalline material is fragmented to yield a nanocrystalline material. Ex. Solid state routes.
  - Produce bulk nanostructured materials
  - Be easily scaled up

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Top-down approach

- Mechanical alloying
- Equal channel angular pressing (ECAP)
- High-pressure torsion
- Accumulative roll bonding
- Nanolithography

Top-down approach

– Mechanical alloying

- High energy ball mills: vibratory mills, planetary mills and attritor mills.

- Used grinding vials and balls of different materials (agate, silicon nitride, zirconia, chrome steel, tungsten carbide)

Mechanical alloying: high energy milling

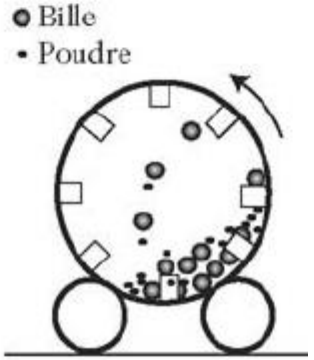
Vibratory ball mill

Mechanical alloying: high energy milling

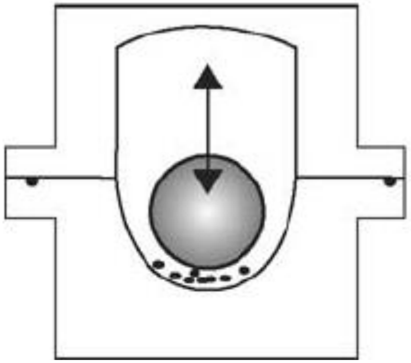
Planetary ball mill

Mechanical alloying: high energy milling

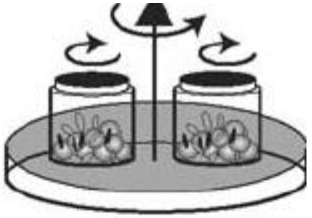
Attritor



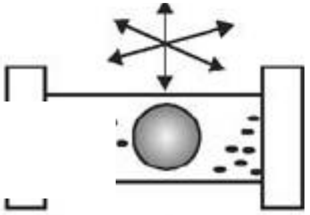
Horizontal mill



1D vibratory



Planetary



3D vibratory

High energy milling: examples

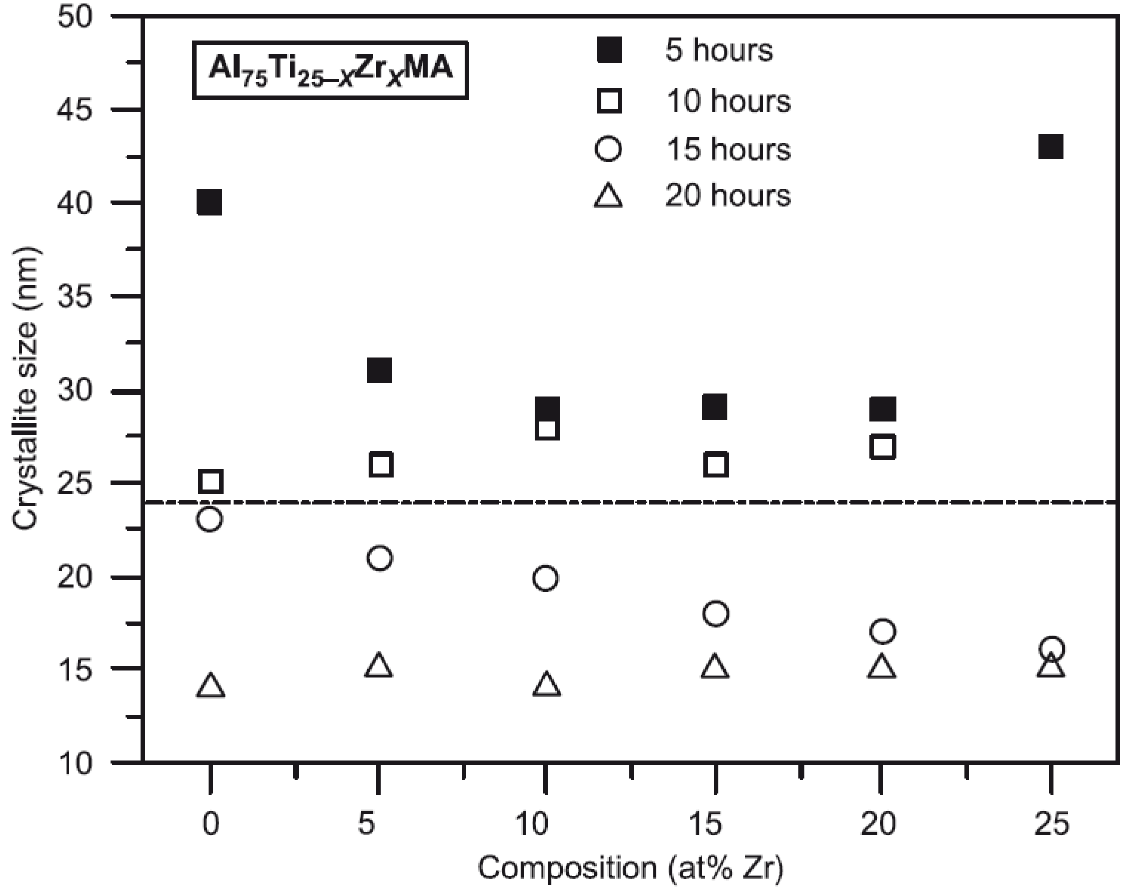
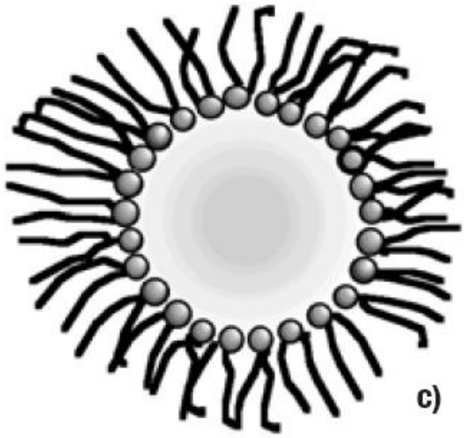


Fig. 3.11 Crystallite size of Al and intermetallic as a function of composition. Nanocrystalline intermetallic compound formation was observed when the crystallite size of Al was below 24 nm. The dotted line demarcates the phase field of mixture of elements and intermetallic compound. (*Source:* BS Murty, IIT Madras).

18 – Colloidal methods and shape anisotropy

- 18.1 Introduction
- 18.2 Surfactants
- 18.3 Reverse micelles: spherical nanoreactors
- 18.4 Factors affecting shape control
  - Colloidal template
  - Anion
  - Molecular adsorption
- 18.5 Conclusion



Colloidal system

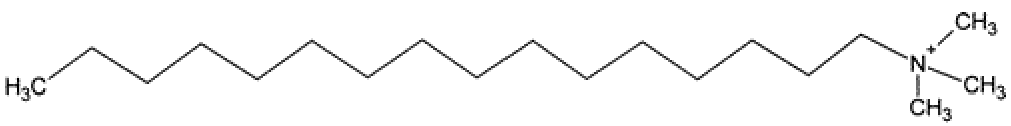
- A multiphase system in which at least one of the phases is composed of particles with sizes less than 1 μm

- Used for synthesizing nanocrystals

Surfactants

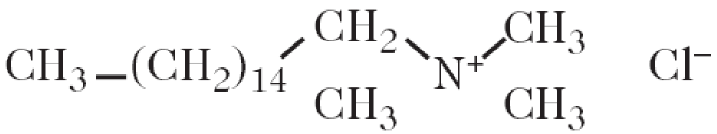
- Surfactants are molecules with a hydrophilic polar head and a hydrophobic hydrocarbon chain

- Examples:
  - Cetyltrimethylammonium bromide (CTAB)



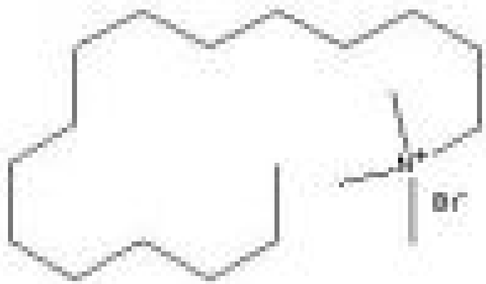
CTAB

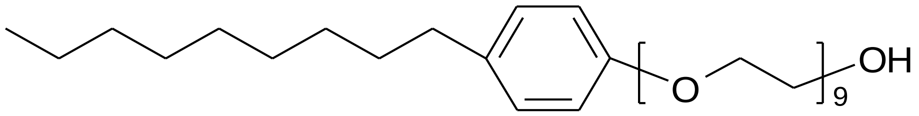
  - Cetyltrimethylammonium chloride (CTAC)



Types of surfactants

- Ionicity $CH_3-(CH_2)_{11}-O-SO_3^-\ Na^+$
  - Anionic
    - Ex.: Sodium dodecylsulfate
  - Cationic
    - Ex.: CTAB
  - Non-ionic
    - Ex.: Polyoxyethylene nonylphenyl ether

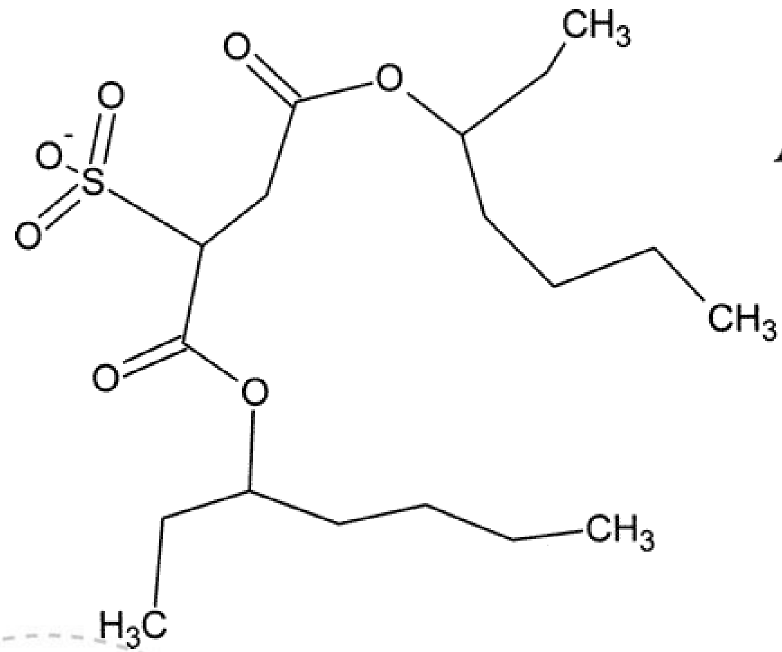




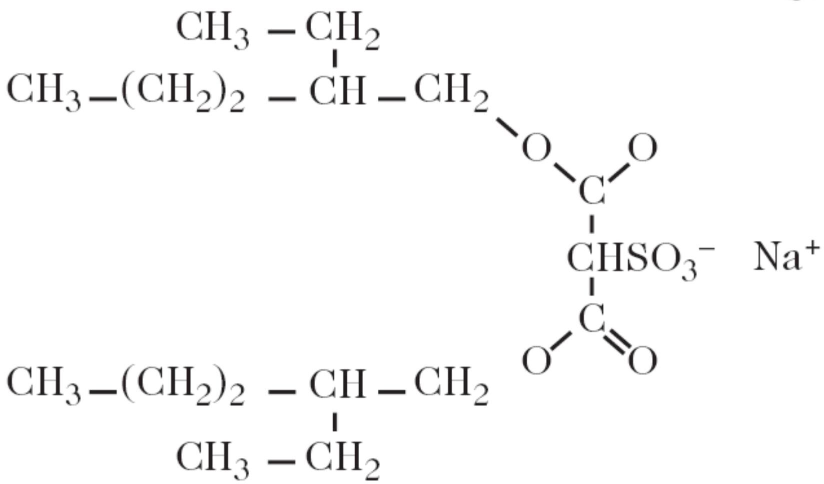
- Branches
  - Single branch
  - Several branches (multibranched)

AOT

- Aerosol OT
- bis(2-ethylhexyl)-sulfosuccinate
- Na^+AOT^-



AOT

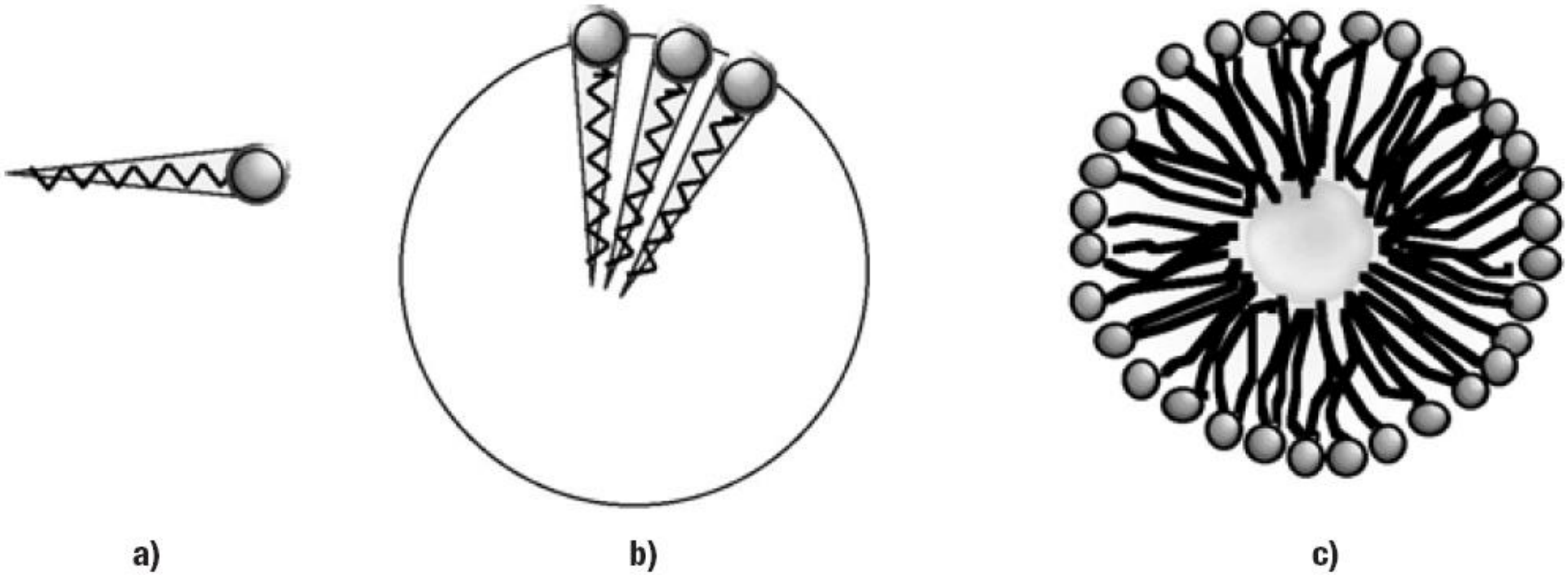


Why surfactants?

- Why and how do we use surfactants?

- What determines the shape and type of aggregate that surfactants produce?

Micelles

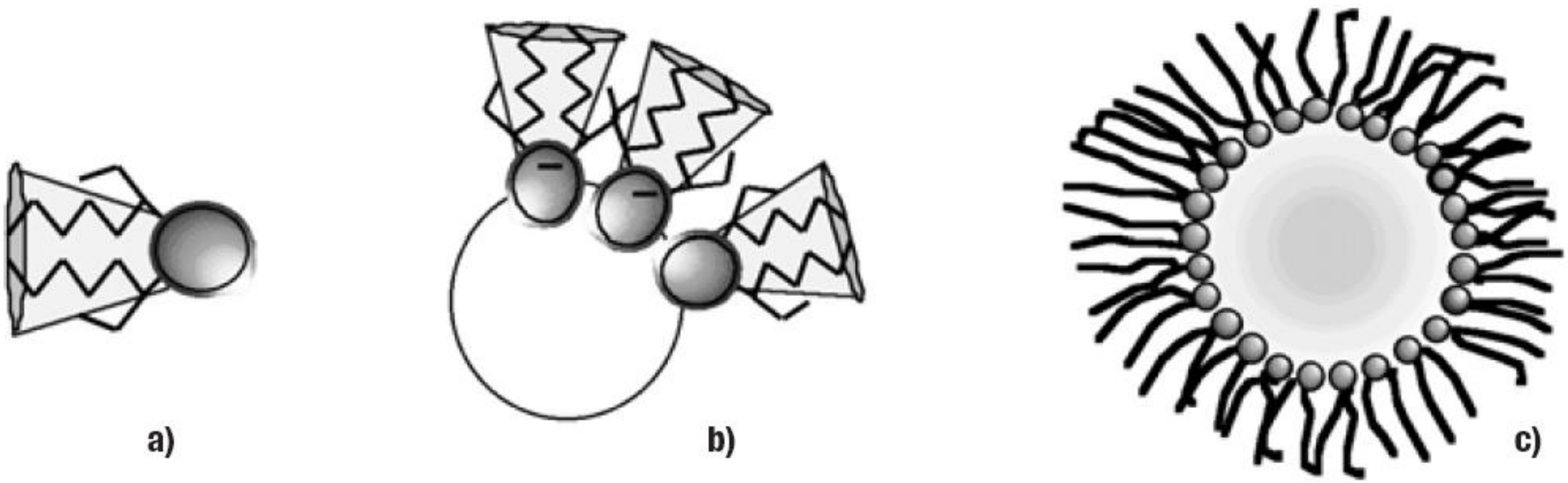


What characterizes a micelle

- Shape and size
- Dynamic system
- Surfactants can leave the aggregate and be replaced by others.

Reverse micelles

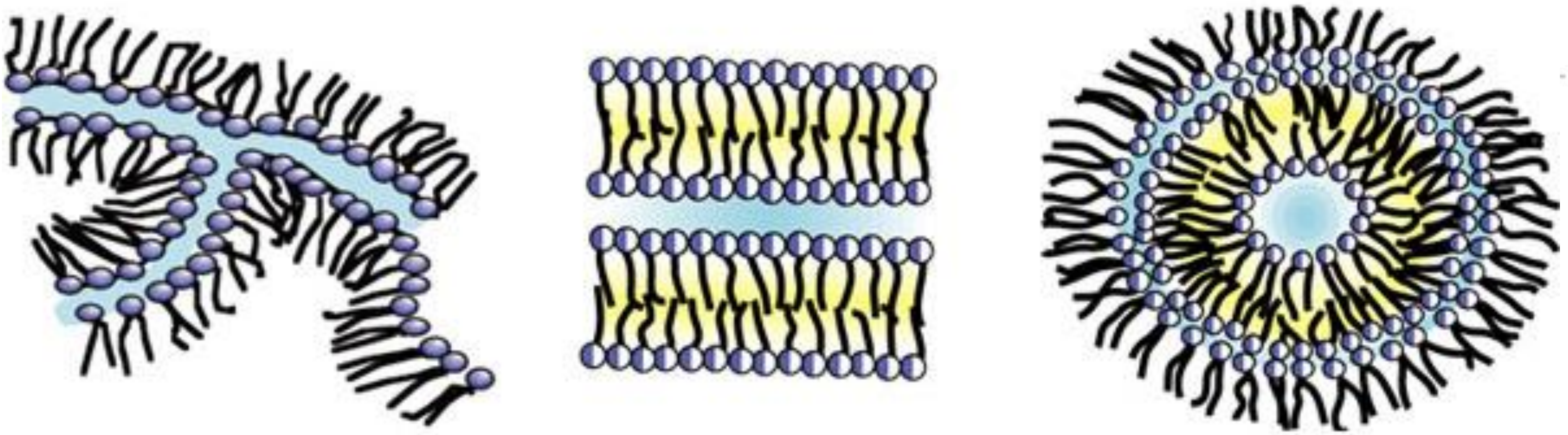
- Also called *inverse* micelles
- Surfactant has a small polar head and a branching hydrocarbon chain (champagne cork shape) → form aggregates like spherical droplets of water in oil



Water-oil-surfactant system

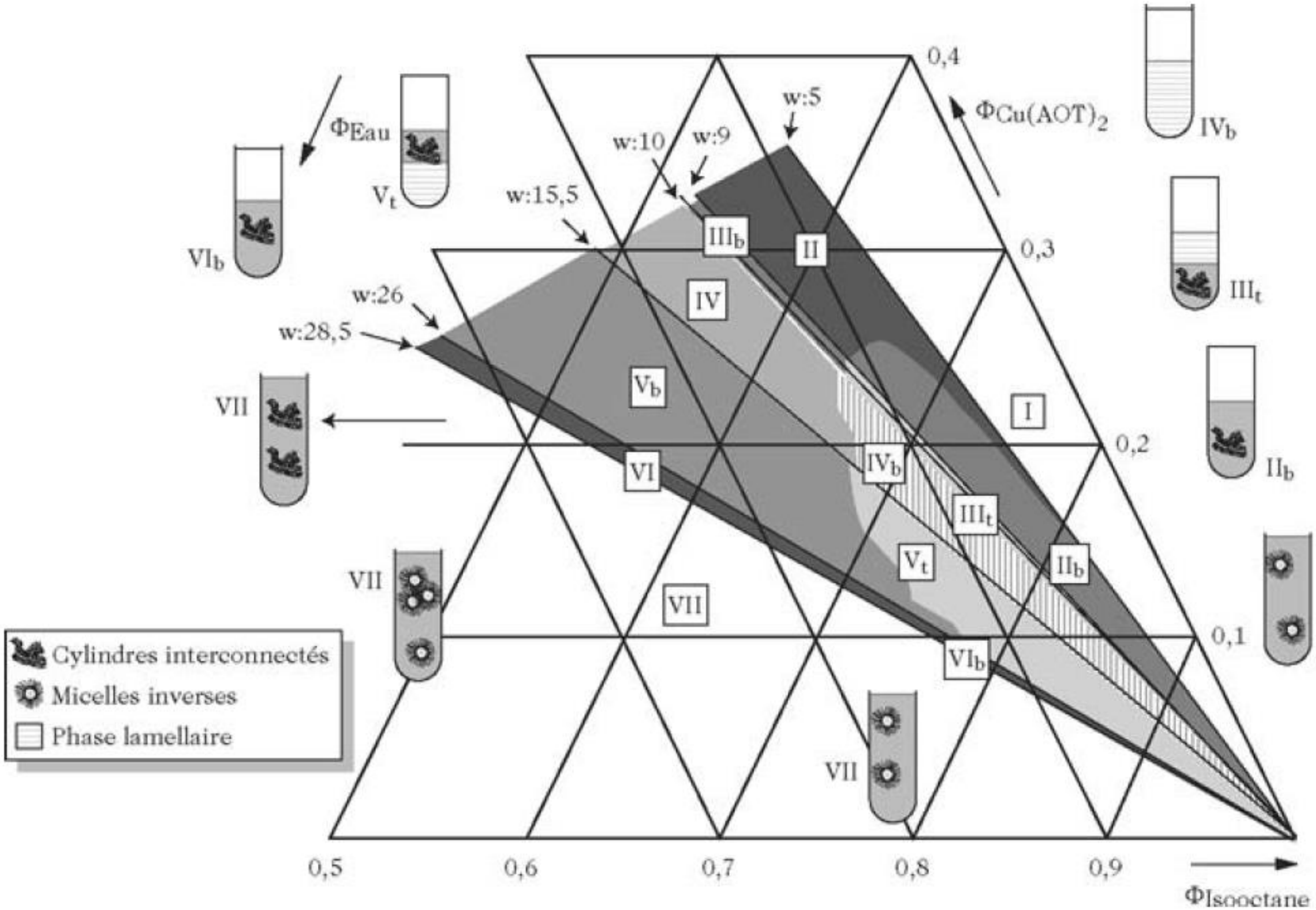
- For surfactants in an oil-rich phase with rather large quantities of water, there are changes in the shape and dimensions of aggregates with the formation of interconnected water channels

- Cylinders
- Lamellar phase
- Onion phase



(a) (b) (c)

Phase diagram

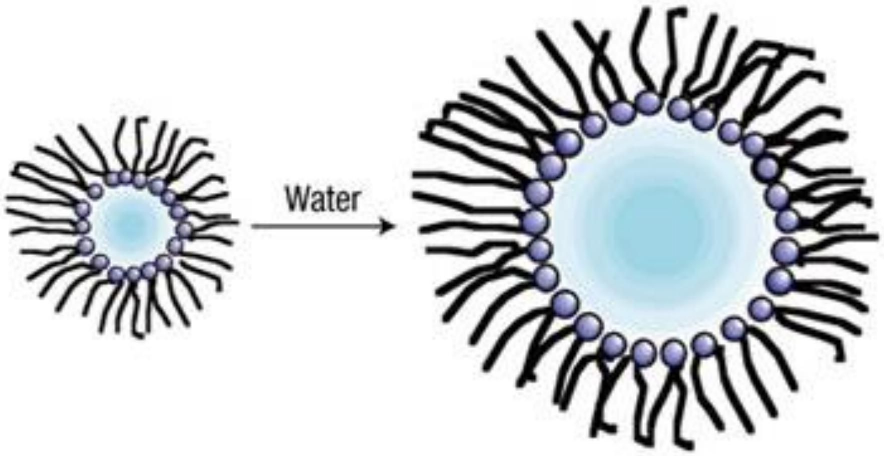


Water content

- The size of reverse micelles varies linearly with the amount of water added to the system, from 4 to 18 nm
- The water content of the system is defined as:

$$w = [H_2O]/[SA]$$

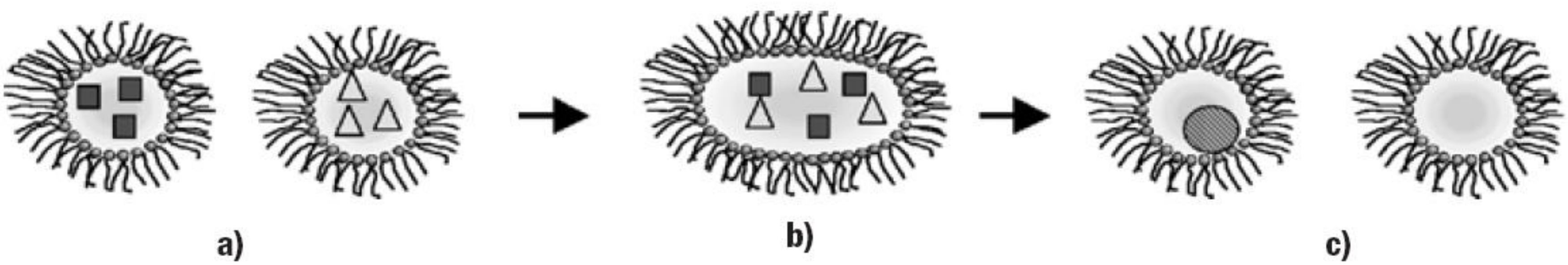
  - [SA] is the surfactant concentration



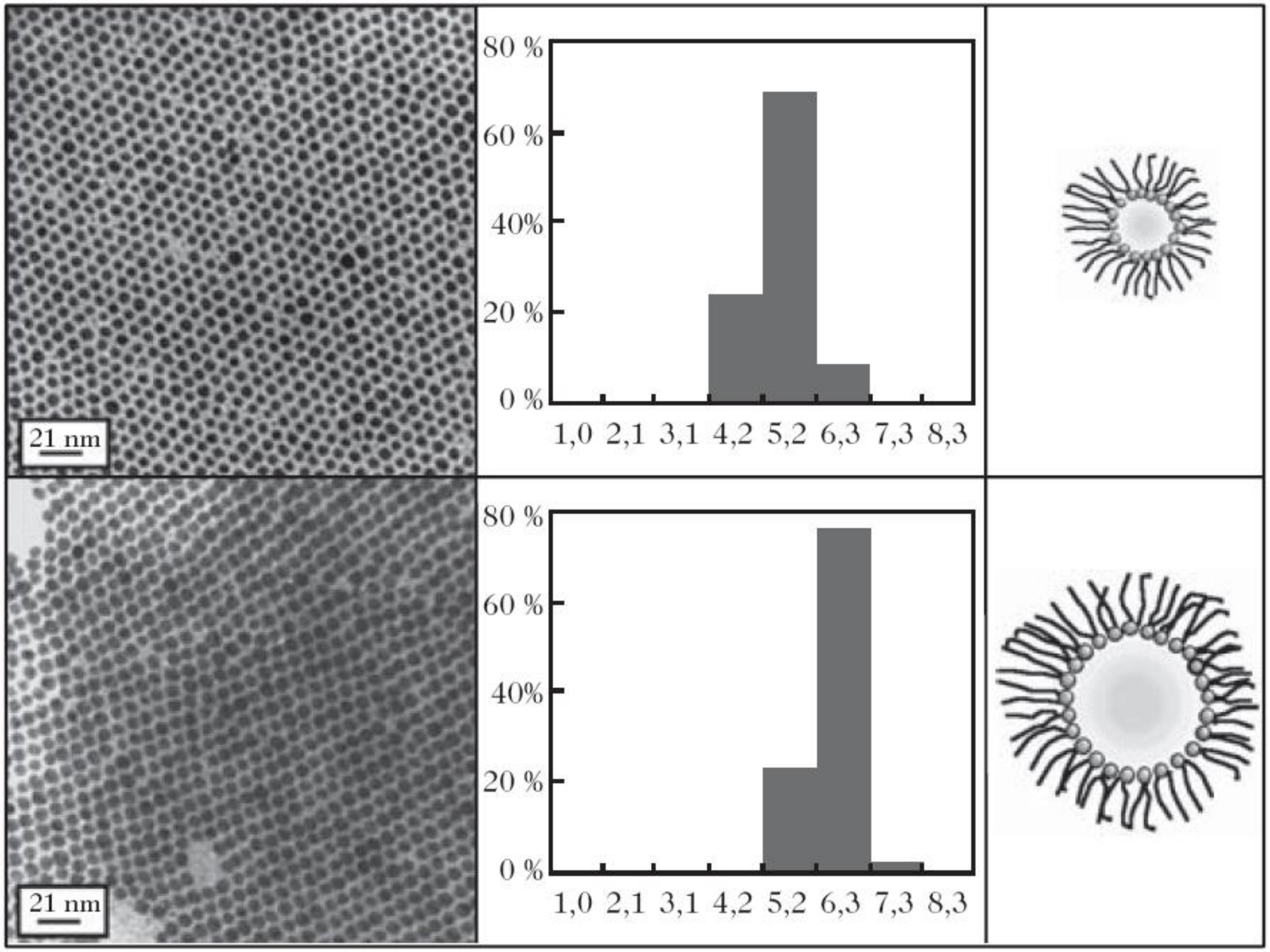
Controlling the size of reverse micelles by water content *w*. (**a**) *w* = 2. (**b**) *w* = 20.

Reactions in reverse micelles

- Brownian motion
- Collision → short-lived dimer
- Exchange of aqueous content
- Reform two reverse micelles
- The products have nearly uniform size and shape
  - In general spherical shape



Size control by adjusting *w*



Water structure

- Low water content ($w < 10$)
  - The water molecules in the micelle core are strongly associated with counterions
  - The water is said to be bound
- Higher water content ($w > 10$)
  - The water is no longer primarily involved in a hydration process and it is said to be free

- Impact on size control
  - 0.6-6 nm reverse micellar size: Similar size of nanocrystals
  - 6-12 nm reverse micellar size: No change in nanocrystal size

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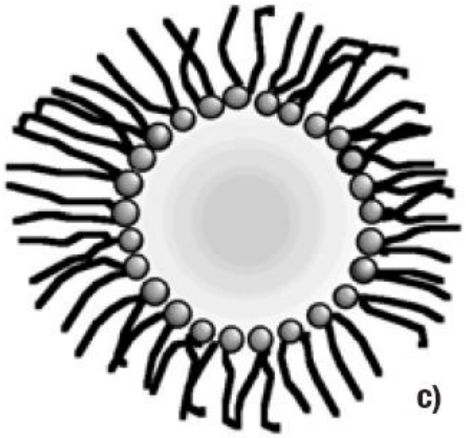

Water structure (recap from last time)

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Synthesis of metals by reduction

- When a reverse micelle solution contains a dissolved metal salt and a second reverse micelle solution containing a suitable reducing agent is added, the metal cations can be reduced to the metallic state
- Reducing agents
  - Sodium borohydride, $NaBH_4$
  - Hydrazine, N_2H_4

- Example: Reduction of H_2PtCl_6 with hydrazine via a $PtCl_4^{2-}$ intermediate:

(1) $2\ PtCl_6^{2-} + N_2H_5^+ \rightarrow 2\ PtCl_4^{2-} + N_2\ (g) + 5\ H^+ + 4\ Cl^-$

(2) $2\ PtCl_4^{2-} + N_2H_5^+ \rightarrow 2\ Pt + N_2\ (g) + 5\ H^+ + 8\ Cl^-$

(1+2) $2\ PtCl_6^{2-} + 2\ N_2H_5^+ \rightarrow 2\ Pt + 2\ N_2\ (g) + 10\ H^+ + 12\ Cl^-$

Table 6. Representative Examples of Nanoparticulate Metals Prepared by Reduction in Microemulsions

metal	starting material	surfactant	reducing agent	reaction conditions	product size (nm)
Co	$CoCl_2$	AOT	$NaBH_4$		<1
Ni	$NiCl_2$	CTAB	$N_2H_4 \cdot H_2O$	pH ~ 13	4
Cu	$Cu(AOT)_2$	AOT	N_2H_4		2–10
	$Cu(AOT)_2$	AOT	$NaBH_4$		20–28
Se	H_2SeO_3	AOT	$N_2H_4 \cdot 2HCl$		4–300
Rh	$RhCl_3$	PEGDE	H_2		3
Pd	$PdCl_2$	PEGDE	$N_2H_4 \cdot H_2O$	pH ~ 7	4
Ag	$AgNO_3$	PEGDE	$NaBH_4$		3–9
Ir	$IrCl_3$	PEGDE	H_2	70 °C	3
Pt	H_2PtCl_6	PEGDE	$N_2H_4 \cdot H_2O$		3
Bi	$BiOClO_4$	AOT	$NaBH_4$	Ar atm	2–10

– PEDGE = pentaethylene glycol dodecyl ether

Crystallinity and oxidation

- Obtained nanocrystals can be amorphous
- Well-crystallized nanoparticles are obtained by using functionalized surfactants
- Metals are easily oxidized if not functionalized to surfactants

Synthesis of metal oxides

- Relies on co-precipitation of one or more metal ions.
- Typically precipitation of the hydroxide
- If the metal cation is insoluble or unstable, hydrolysis of a suitable precursor can be used:

$$Ti(O^{i}Pr)_4 + 2\ H_2O \rightarrow TiO_2 + 4\ (^{i}Pr\text{-}OH)$$

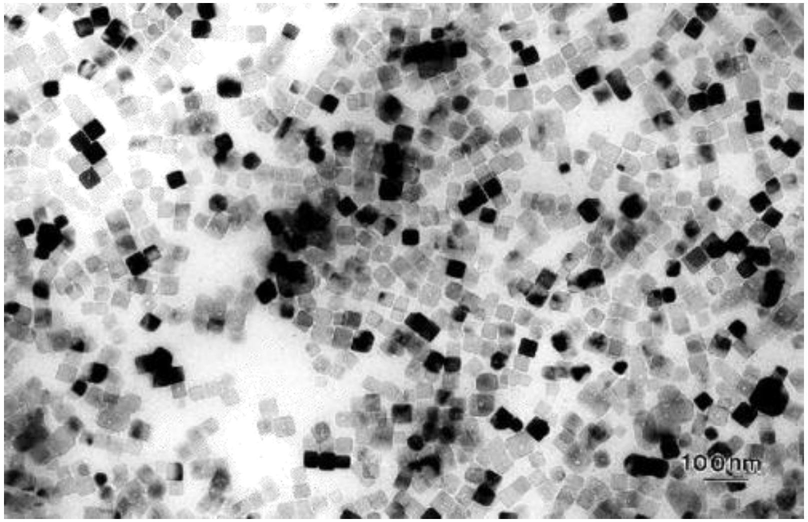
Table 7. Survey from the Literature of Oxides Prepared from Microemulsions

oxide	starting material	surfactant	precipitating agent	reaction conditions	product size (nm)	ref
$LiNi_{0.8}Co_{0.2}O_2$	$LiNO_3$ $Ni(NO_3)_2$ $Co(NO_3)_2$	NP-10	kerosene	calcined 400–800 °C	19–100	441
Al_2O_3	$AlCl_3$	Triton X-114	NH_4OH	calcined 600–900 °C	50–60	437
TiO_2	$Ti(O^iPr)_4$	AOT	H_2O		20–200	434
$Mn_{1-x}Zn_xFe_2O_4$	$Mn(NO_3)_2$ $Zn(NO_3)_2$ $Fe(NO_3)_3$	AOT	NH_4OH	calcined 300–600 °C	5–37	435
Fe_3O_4	$FeCl_2$ $FeCl_3$	AOT	NH_4OH		~2	443
Fe_3O_4	$FeSO_4$	AOT	NH_4OH		10	431
$CoCrFeO_4$	$CoCl_2$ $CrCl_3$ $Fe(NO_3)_3$	SDS	CH_3NH_2	calcined 600 °C	6–16	444
$CoFe_2O_4$	$CoCl_2$ $FeCl_3$	SDS	CH_3NH_2	dried 100 °C	6–9	445
$Ni_{1-x}Zn_xFe_2O_4$	$Ni(NO_3)_2$ $Zn(NO_3)_2$ $Fe(NO_3)_3$	AOT	NH_4OH	calcined 300–600 °C	5–30	435
CuM_2O_5 (M = Ho, Er)	$Cu(NO_3)_2$ $NO(NO_3)_3$ $Er(NO_3)_3$	CTAB	$(NH_4)_2CO_3$	calcined 900 °C	25–30	440
$Y_3Fe_5O_{12}$	$Y(NO_3)_3$ $Fe(NO_3)_3$	Igepal CA-520	NH_4OH + $(NH_4)_2CO_3$	calcined 600–1000 °C	3	446
$YBa_2Cu_3O_{7-\delta}$	$Y(OAc)_3$ $BaCO_3$ $Cu(OAc)_2$	Igepal CA-430	oxalic acid		3–12	436
SnO_2	$SnCl_4$	AOT	NH_4OH	calcined 600 °C	30–70	447
$BaFe_{12}O_{19}$	$Ba(NO_3)_2$ $Fe(NO_3)_3$	CTAB	$(NH_4)_2CO_3$	calcined 950 °C	5–25	439, 442
CeO_2	$Ce(NO_3)_3$	CTAB	NH_4OH	calcined 500–700 °C	6–10	448

$KMnF_3$

- Mixing two solutions of reverse micelles made from CTAB/butanol/octane, one containing $MnCl_2$ in the aqueous core and the other containing KF, cubic nanocrystals of $KMnF_3$ are produced:

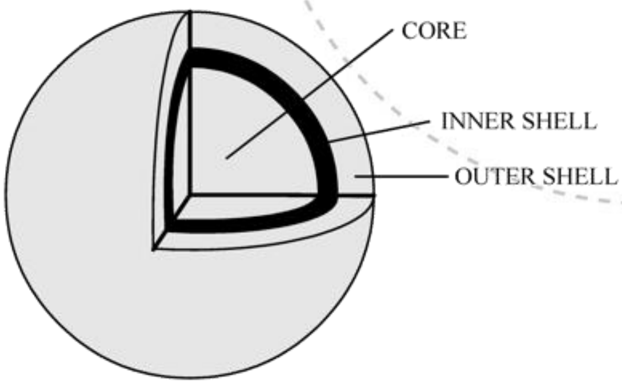
$$MnCl_2\ (aq) + KF\ (aq) \rightarrow KMnF_3\ (s) + 2\ KCl\ (aq)$$



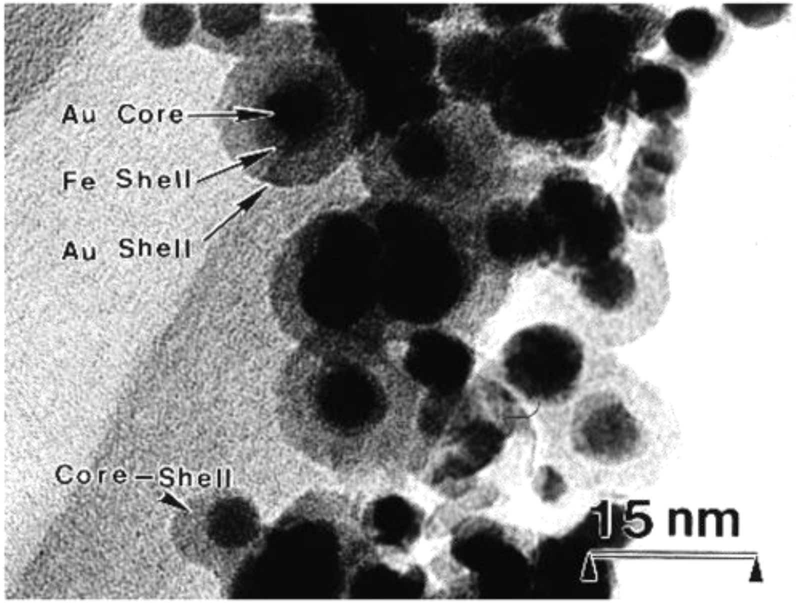
TEM image of nanocrystalline $KMnF_3$.

Core-shell structures

- Successive metal reduction
- Au-Fe-Au onion-type structure



(You should read this section of the review article on your own, p 3928-3929.)



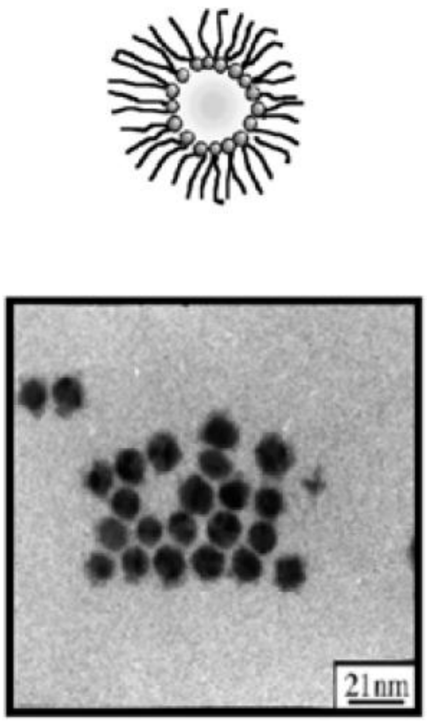
TEM image and schematic of an onion structure.

Shape control

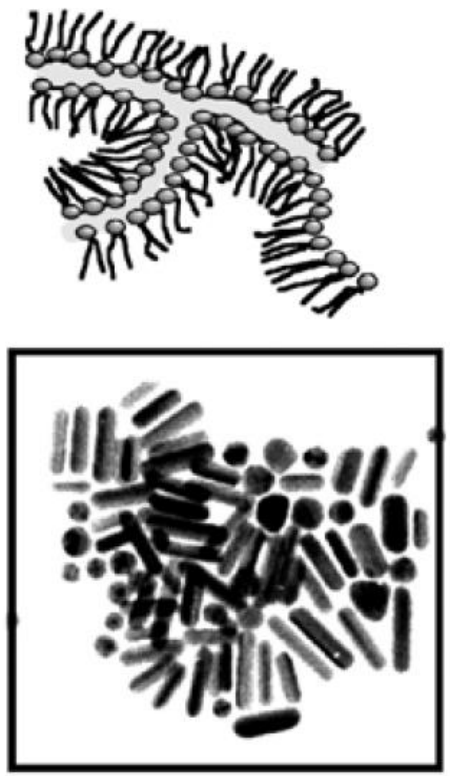
- Reverse micelles in general result in spherical nanocrystals.

- Can cylindrical / lamellar / onion surfactant structures be used as templates for obtaining non-spherical nanocrystals?

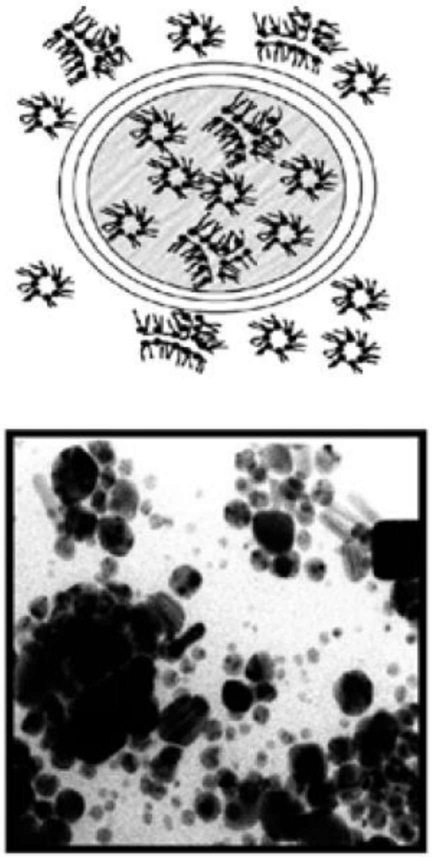
- Metastable structures are possible.



a)

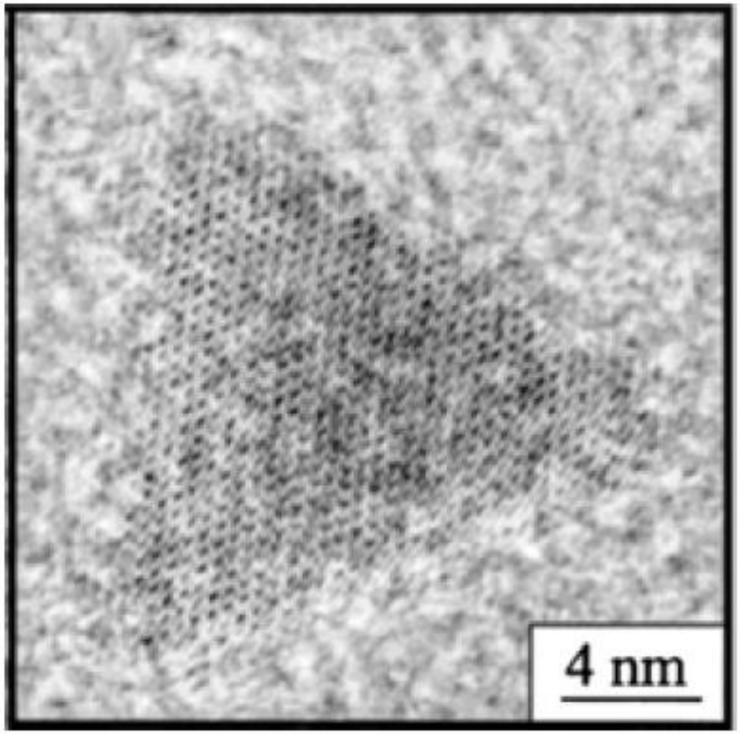


b)



c)

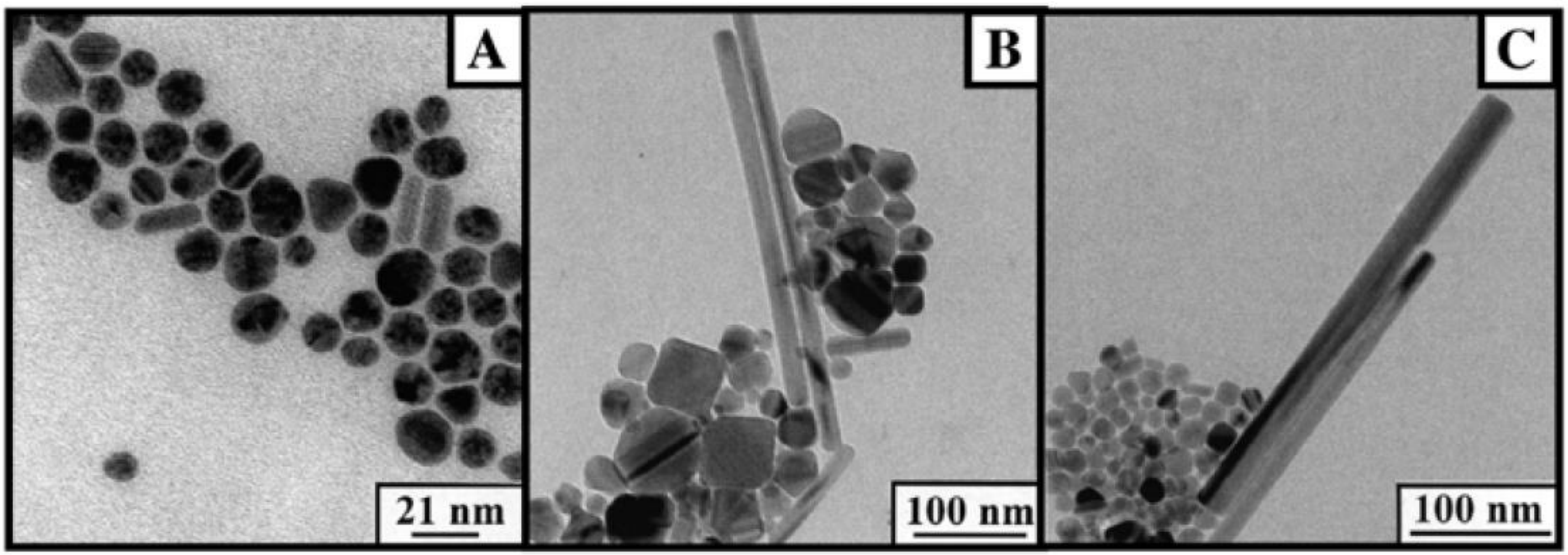
- The role of the template is not as clear as all this would suggest
- Adsorption of ions or molecules must also be taken into account
  - ($KMnF_3$ cubic nanocrystals mentioned previously)



Triangular CdS nanocrystal obtained using a reverse micelle system.

Effect of anions on nanocrystal growth

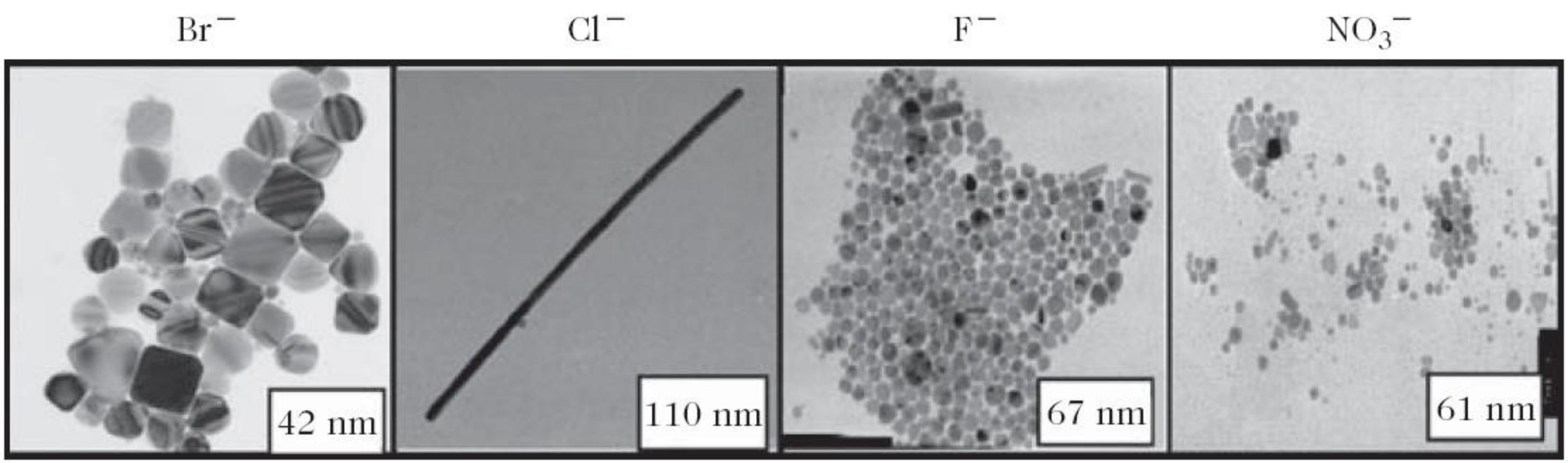
- Ternary system $Cu(AOT)_2$–water–isooctane
- Interconnected cylinder region
- What happens when NaCl is added?



[NaCl] = 0 M | [NaCl] = 5×10^{-4} M | [NaCl] = 1.1×10^{-3} M

What if NaBr is added instead?

- Add NaBr → nanocubes
  - Size does not vary with the bromine ion concentration
- Add NO_3^- → a whole range of nanocrystal shapes and sizes is obtained
- Add F^- → small cubes



Effect of different anions on the shape of copper nanocrystals.

Learning objectives chapter 18

- Define surfactant, micelle, reverse micelle
- Mention types of surfactants
- Describe water-oil-surfactant phases
- Explain synthesis using reverse micelles with different content
- Explain how size control of nanoparticles is obtained by this synthesis method
- Understand that the anions are dominant in the formation of anisotropically shaped nanocrystals

- Be able to use this knowledge to suggest a synthesis route for simple compounds