ETH
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Swiss Federal Institute of Technology Zurich

PARTICLE-STABILIZED FOAMS AND THEIR POTENTIAL APPLICATIONS

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422. $\gamma = 5\%$ wt% ÷ 5

Al_2O_3 200 g
Urea (0,32) 0,64 g
H_2O 35 g + 3 g
Prop. ac. (?) 0,8 g

29,53 – 100%
50,13 – 56%

Urease Amount per g Al_2O_3 $\frac{1 \cdot 100}{61000} = 0.0032$ g urease

50 14
0.64
38
0.8
x

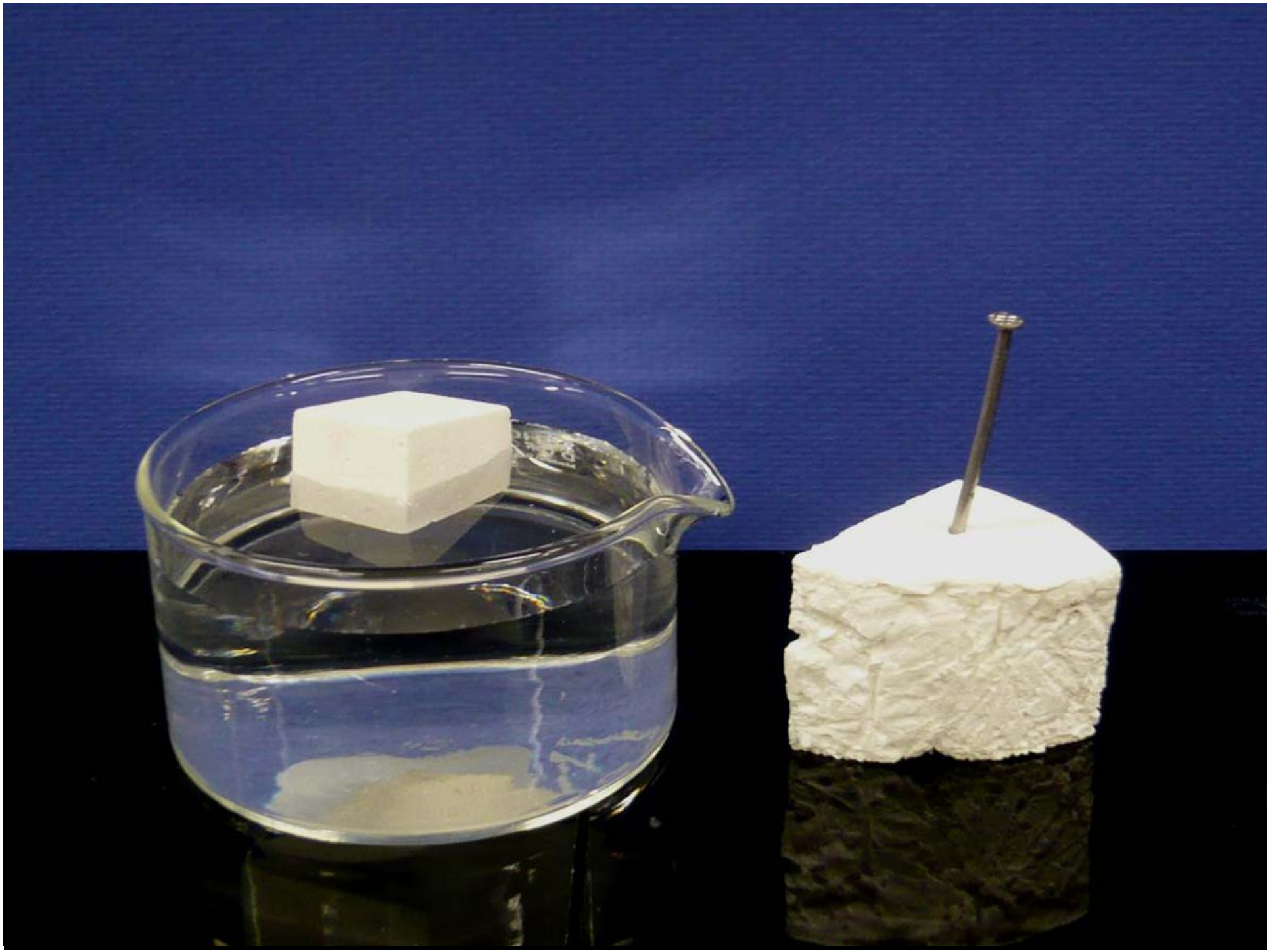
89.58 1x – 100%
50 14 – 55% ⇒ 100% – 91.16 → x = 1.58 g H_2O

⇒ 0.0032 g urease in 1.58 g H_2O

200 g – 100%
0,8 – 0,4% wt% t. 10%

$\frac{0,8\,g}{40\,ml} \quad \frac{1000\,ml}{1\,l} \quad \frac{1\,mol}{174} = 0,27\ mol/l.$

422



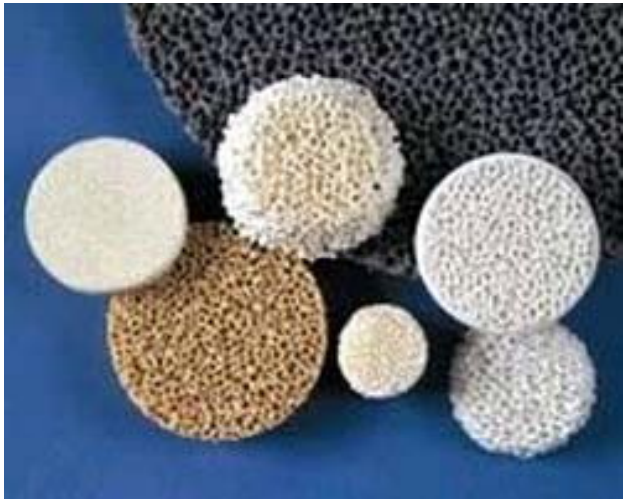
APPLICATIONS OF POROUS CERAMICS

Advantages

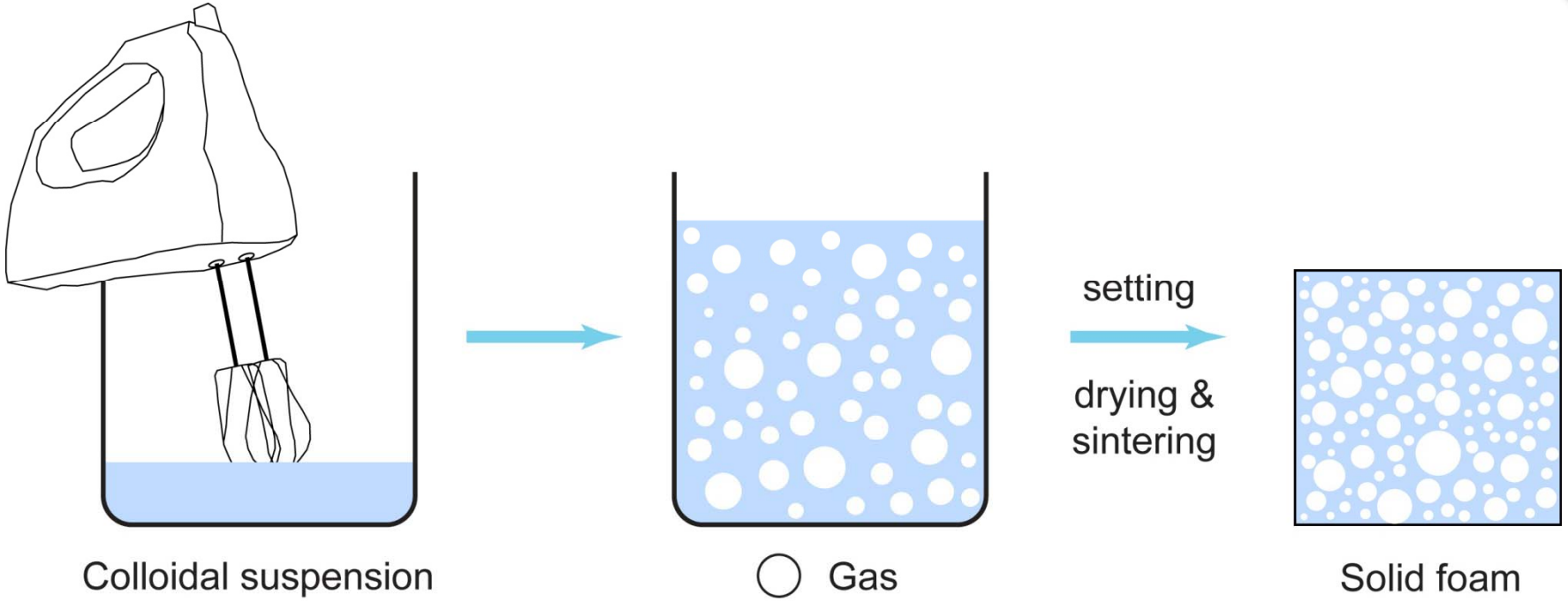
- thermal and corrosion resistance
- low density
- low thermal conductivity
- controlled permeability
- high surface area
- …

Applications

- high-temperature thermal insulation
- filters for molten metals, exhaust gases
- catalyst carriers
- bone grafts
- lightweight materials
- …



DIRECT FOAMING

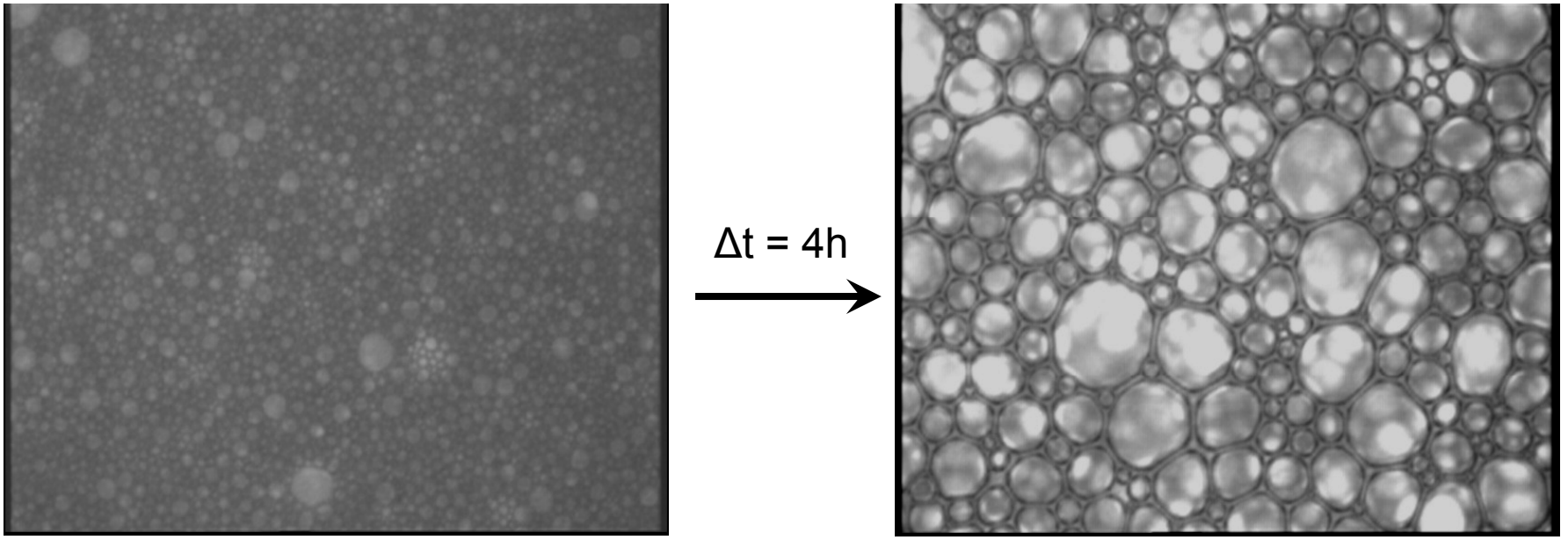


but

excessive coarsening in the wet state due to

- Ostwald ripening (difference in Laplace pressures)
- drainage
- coalescence of single bubbles

COARSENING OF SURFACTANT-STABILIZED FOAMS



How can the foam stability be improved?

PICKERING EMULSIONS

W. Ramsden. “Separation of solids in the surface-layers of solutions and 'Suspensions'. Preliminary Account.”, *Proceedings of the Royal Society,* 72[479], 156-164,**1903**.

S. U. Pickering. “Emulsions”, *Journal of the Chemical Society*, 91, 2001-2021,**1907**.

Percival Spencer Umfreville Pickering
(1858 – 1920)

nourhood of the paramn globules.

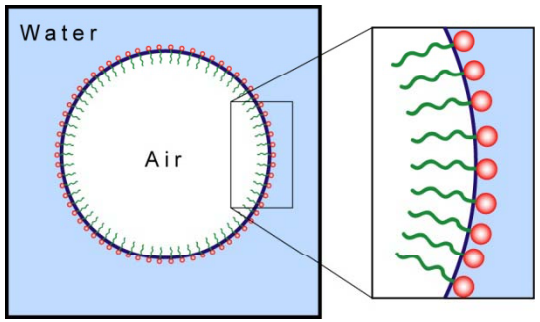
Apparently, a precipitate consisting of any insoluble substance which is wetted more easily by water than by oil, if in a sufficiently fine state of division, will equally act as an emulsifier, and in some cases it is possible under a microscope to see the coating of solid

Besides the facility and certainty with which these emulsions can be made, they possess the advantage of being much more permanent than emulsions made with soap. No single instance has yet occurred in which any one of them has de-emulsified spontaneously. Also they can be mixed with caustic soda (2 per cent. being

- any fine particles are able to stabilize oil-in-water emulsions
- enhanced stability compared to surfactant-stabilized emulsions

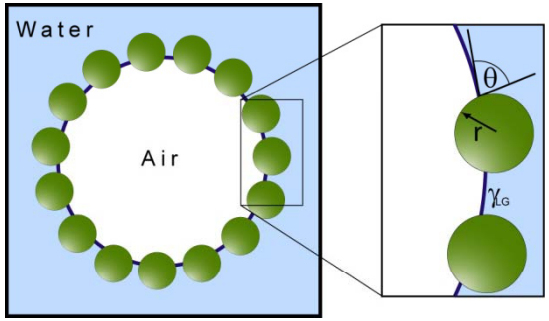
STABILIZATION OF THE AIR-WATER INTERFACE

long-chain surfactants



$$\Delta G_{surfactant} \approx 1-3kT$$

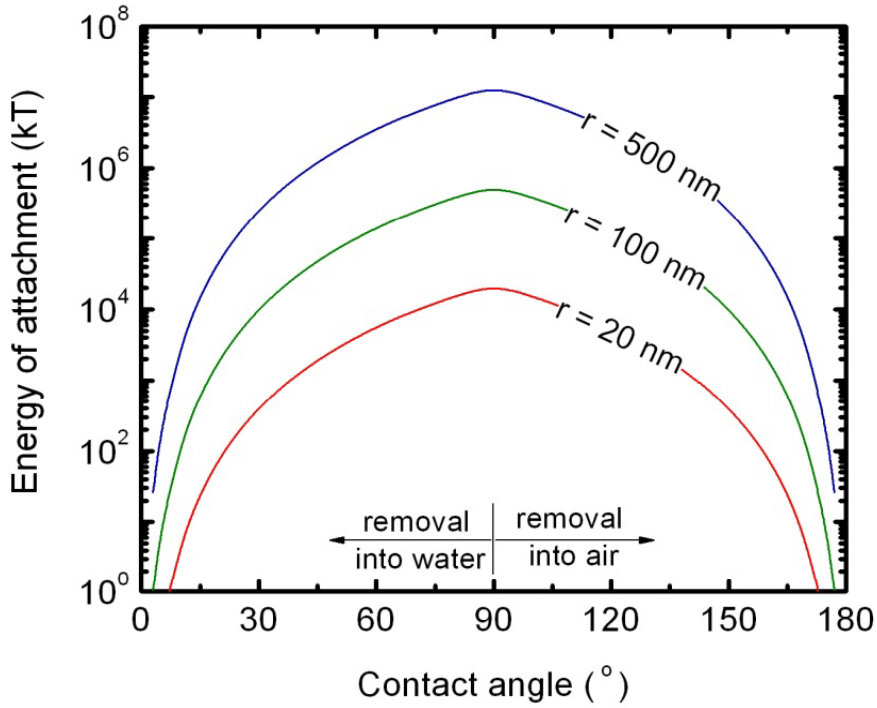
particles



$$\Delta G_{particle} \approx 10^3 - 10^5 kT$$

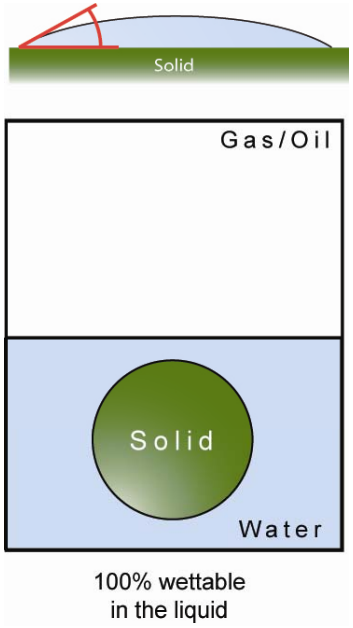
Free energy gain by loosing an area of fluid-gas interface

$$\Delta G_{particle} = \pi r^2 \gamma_{LG} (1 \pm \cos\theta)^2$$

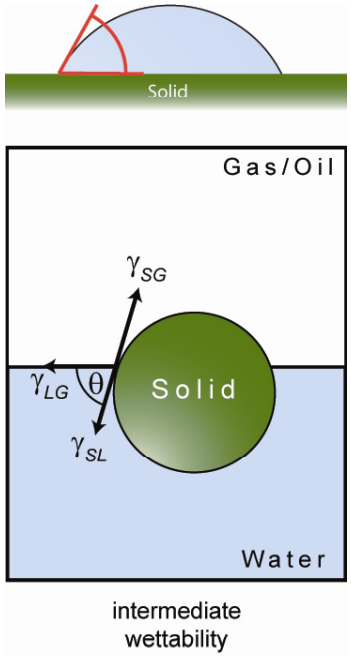


- particles can be surface active, but are not amphiphilic (expect janus particles)
- particles strongly held at interface, enhanced stability of the foam

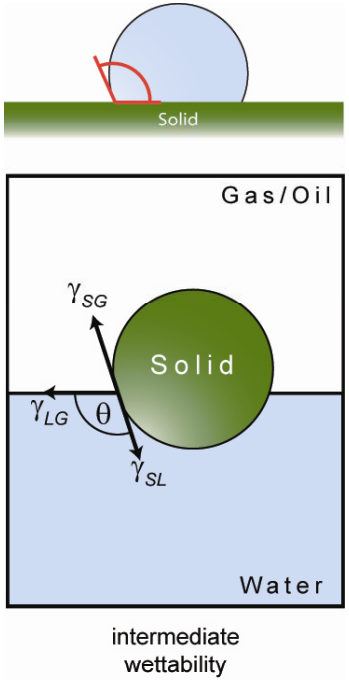
PARTICLES IN MIXTURES OF IMMISCIBLE PHASES



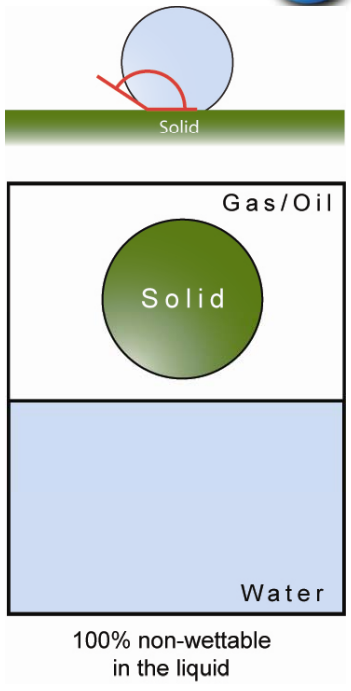
100% wettable in the liquid



intermediate wettability



intermediate wettability



100% non-wettable in the liquid

Oxides:

Al_2O_3, ZrO_2, SiO_2, $Ca_3(PO_4)_2$, hydroxyapatite, …

condition to obtain

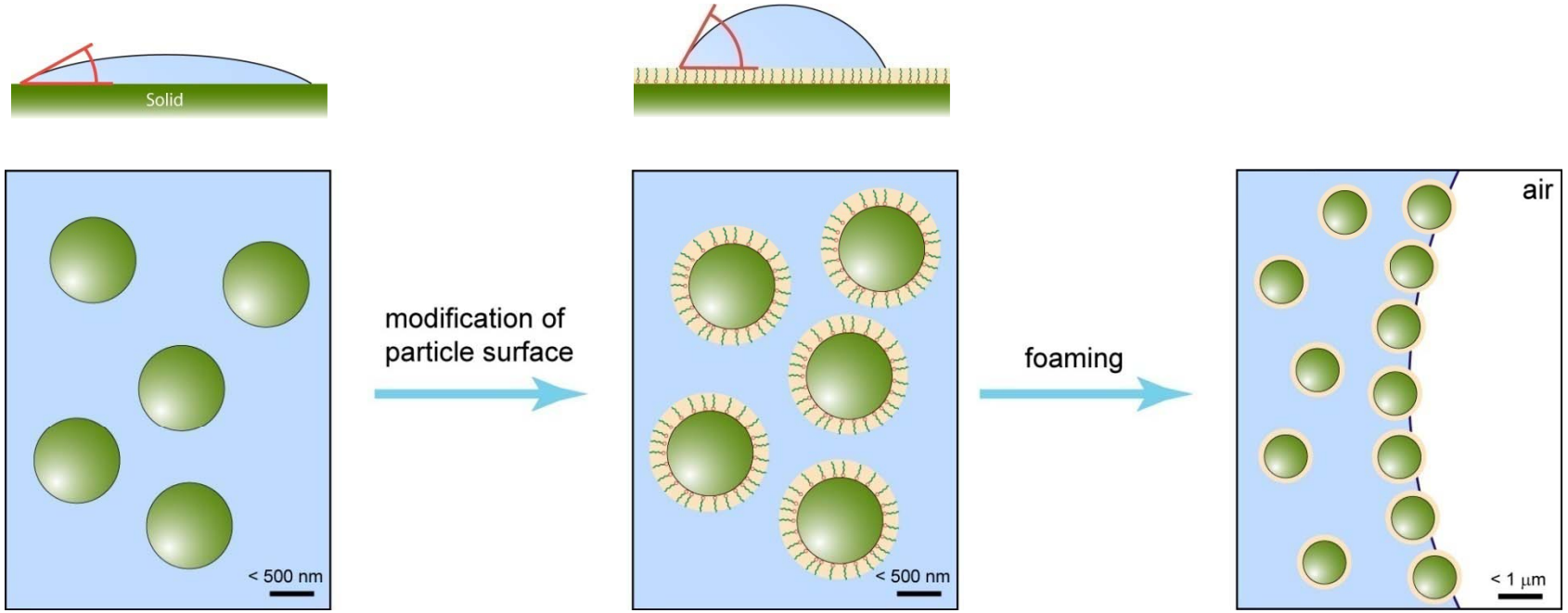
FOAMS or O/W EMULSIONS

MISTS or W/O EMULSIONS

Polymers:

Polyethylene (PE), Polyvinyldifluoride , Teflon (PTFE), …

IN-SITU HYDROPHOBIZATION OF PARTICLES

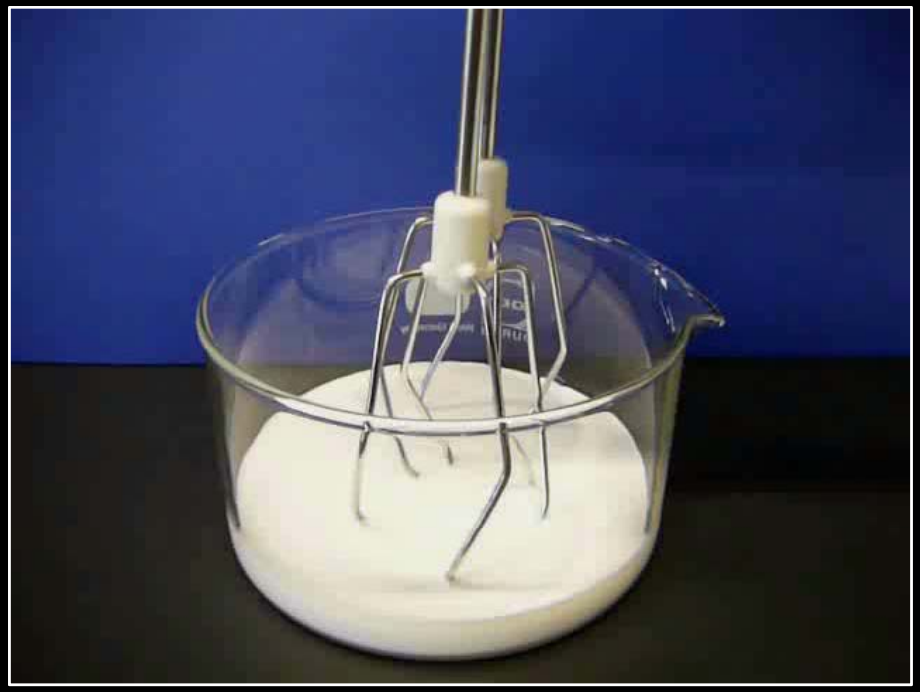


short-chain amphiphilic molecules as surface modifiers

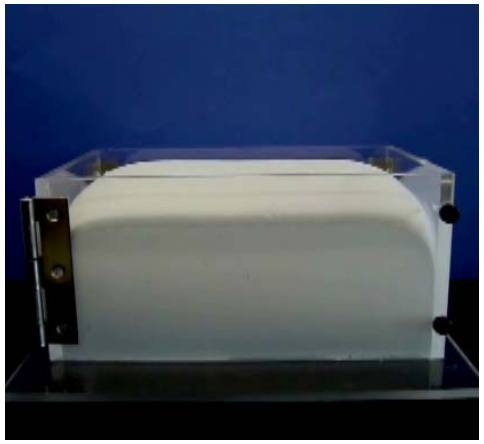
→ high solubility in water
→ high concentration of modified particles
→ stabilization of large interfacial area

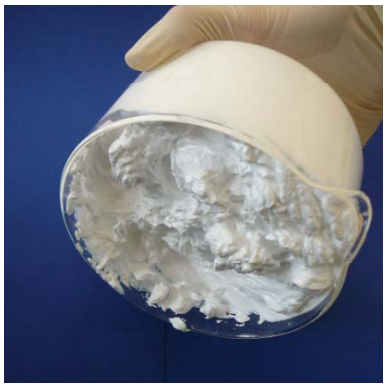
Gonzenbach et al. *Angewandte Chemie-International Edition*, **2006**.

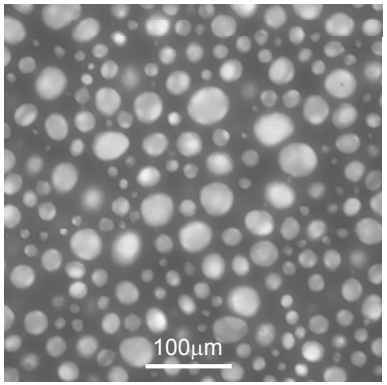
THE FOAMING PROCESS

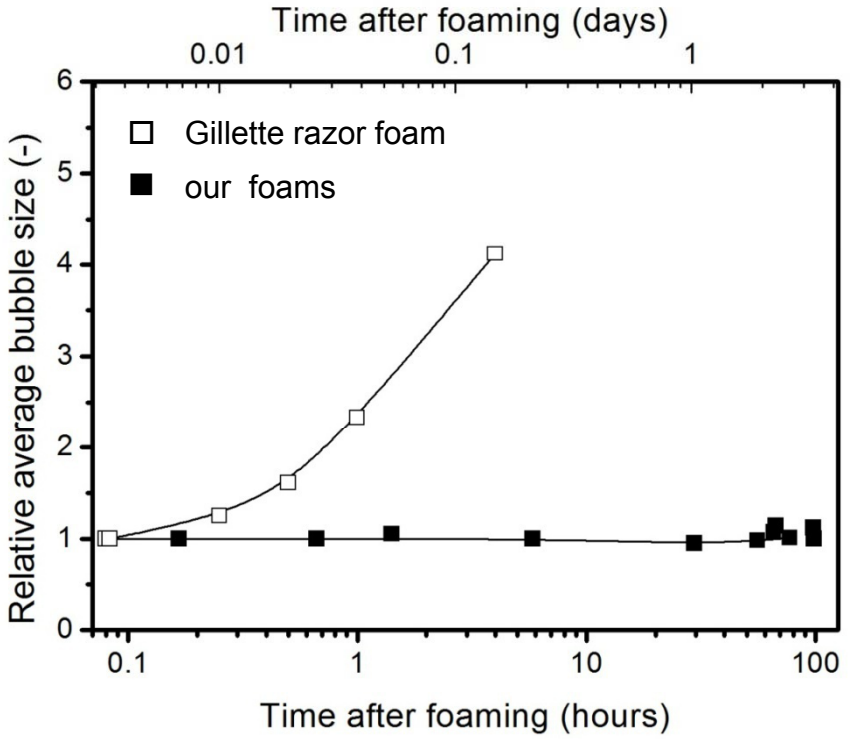


STABILITY OF THE WET FOAMS



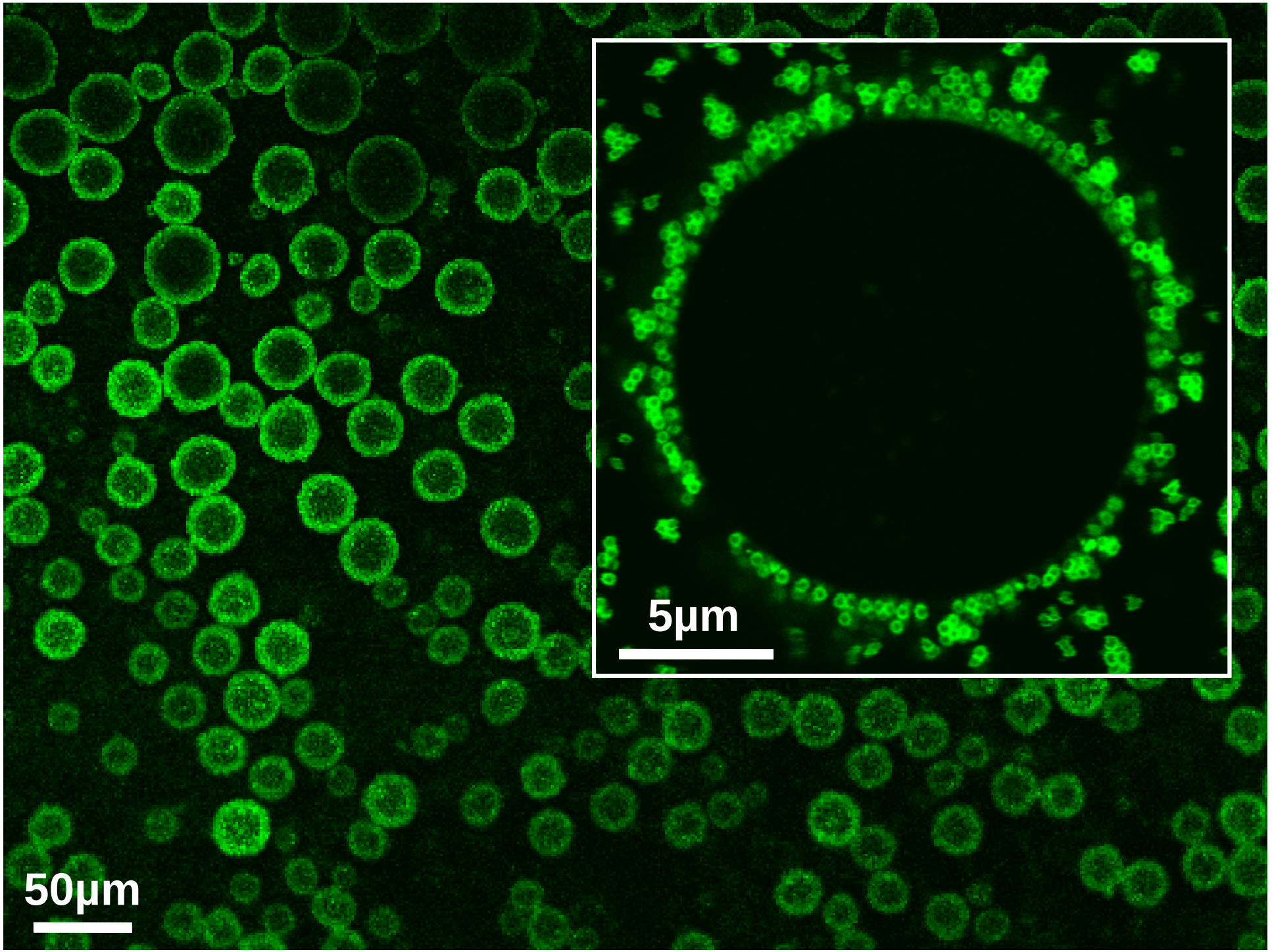






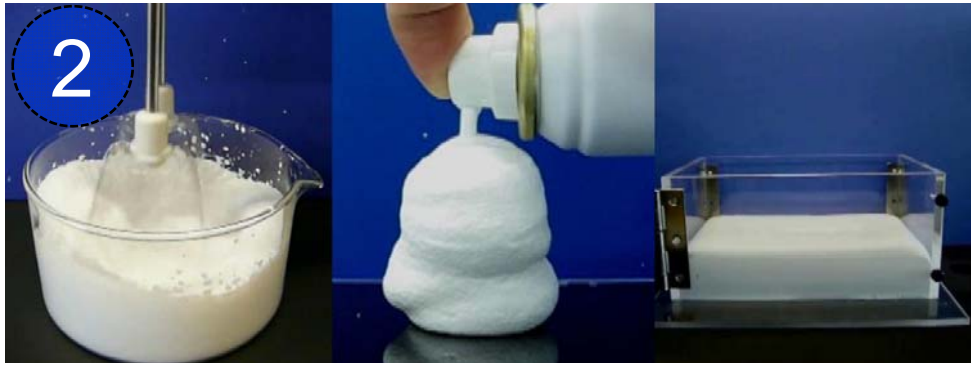
- Suspension homogeneously foamed throughout the whole volume
- Improved wet foam stability compared to state-of-the-art foams

Gonzenbach et al., Journal of the American Ceramic Society, **2007**.


5μm
50μm

FOAM PROCESSING

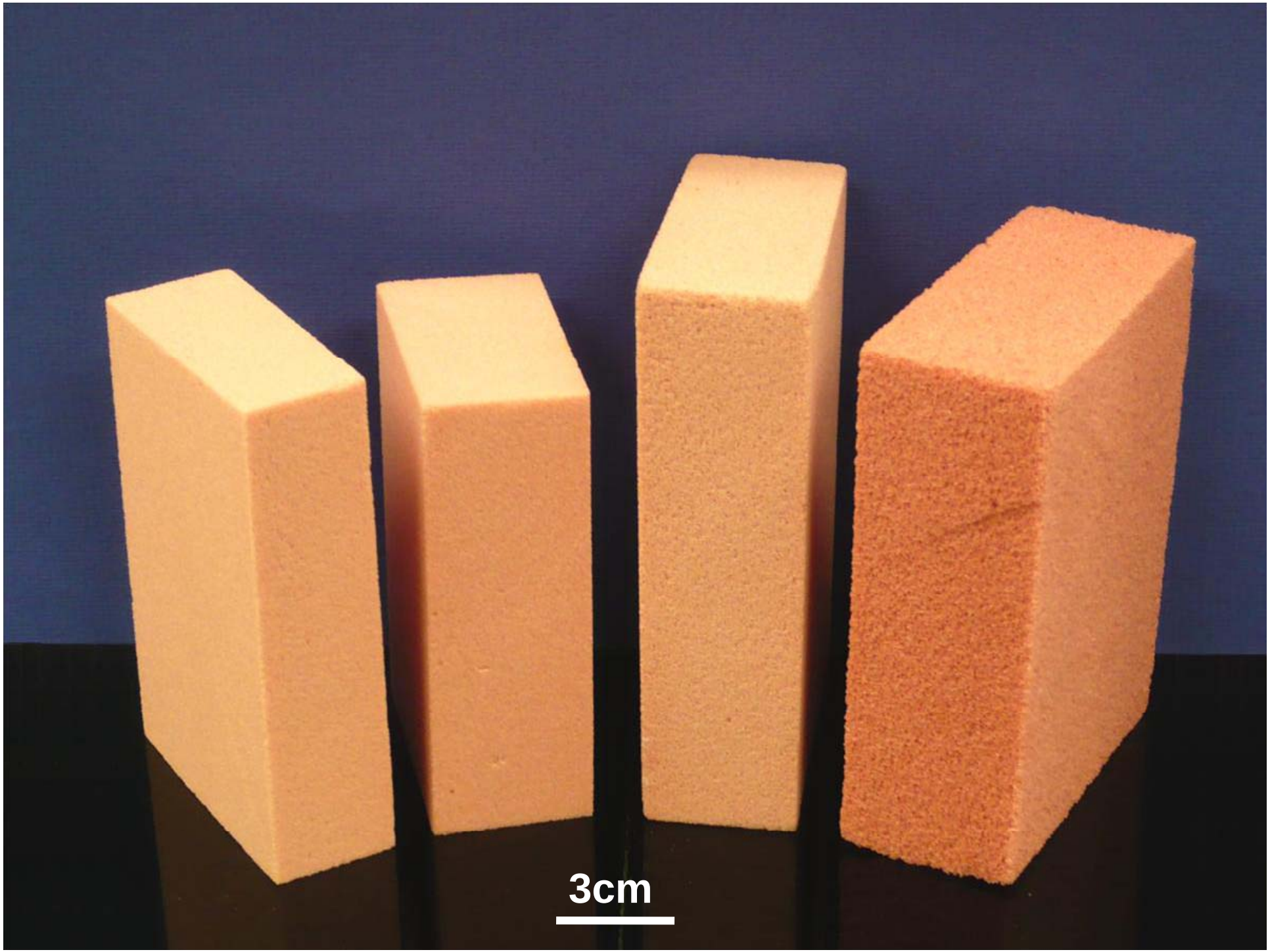
suspension preparation

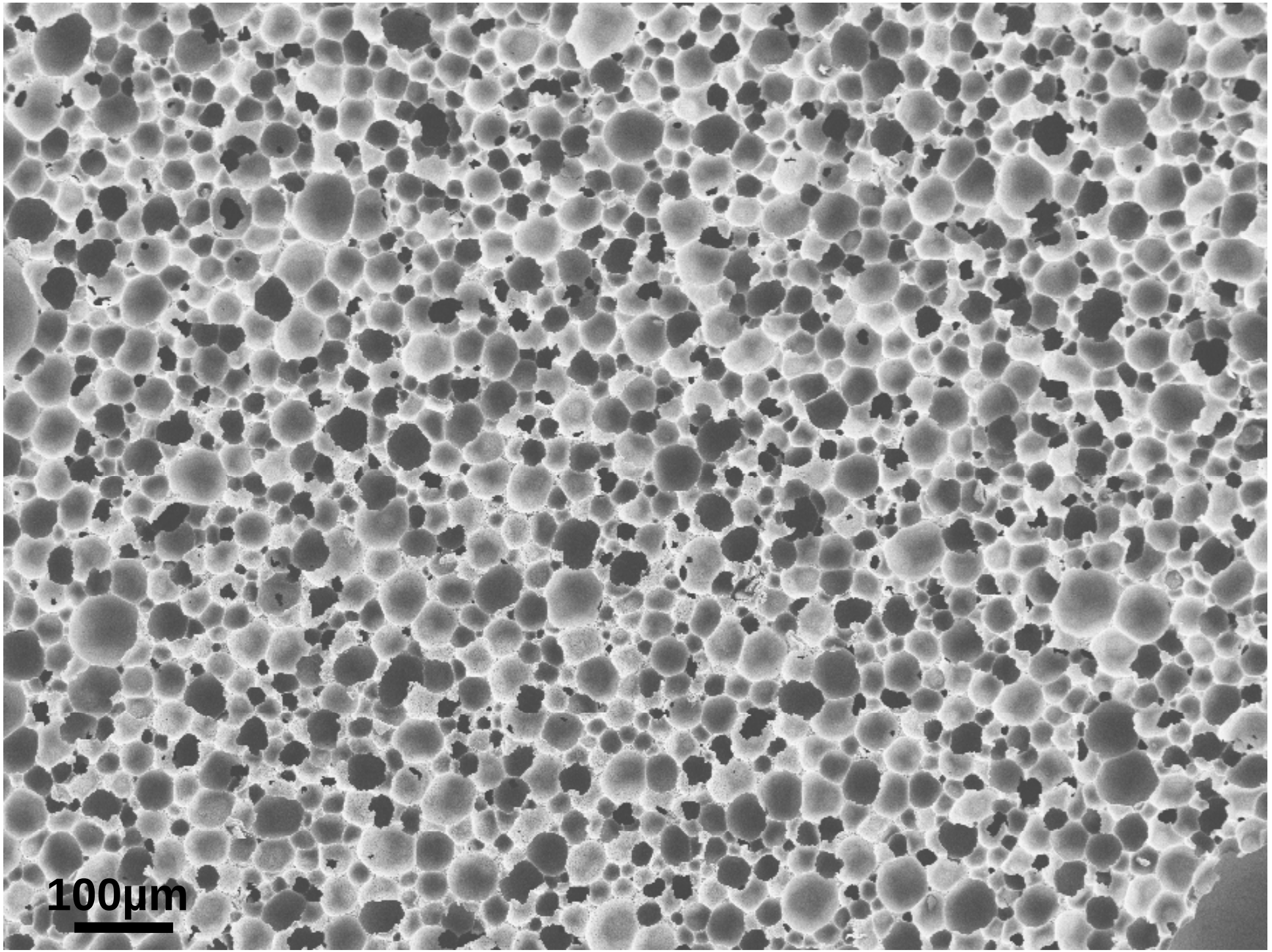


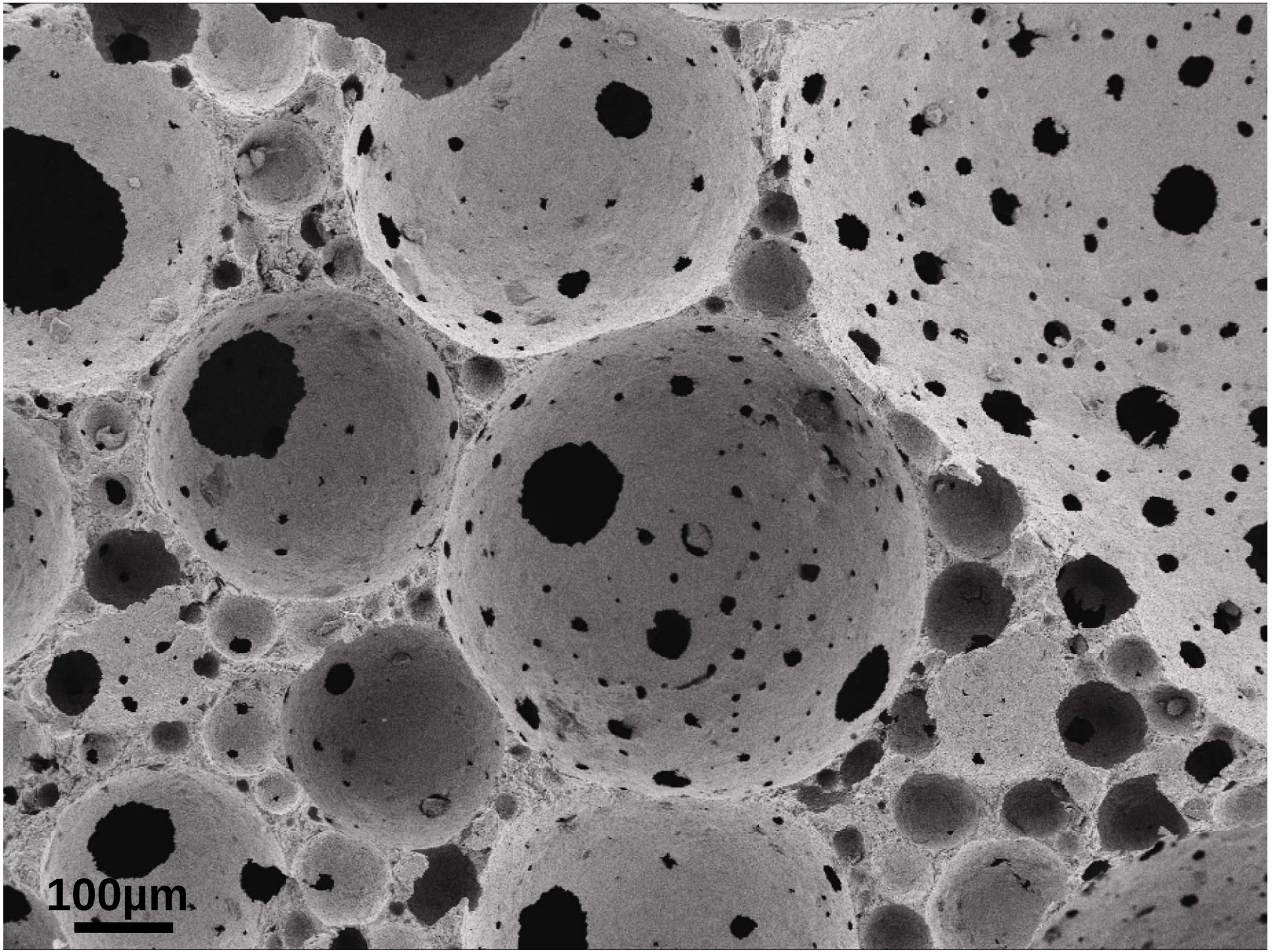
foaming

drying

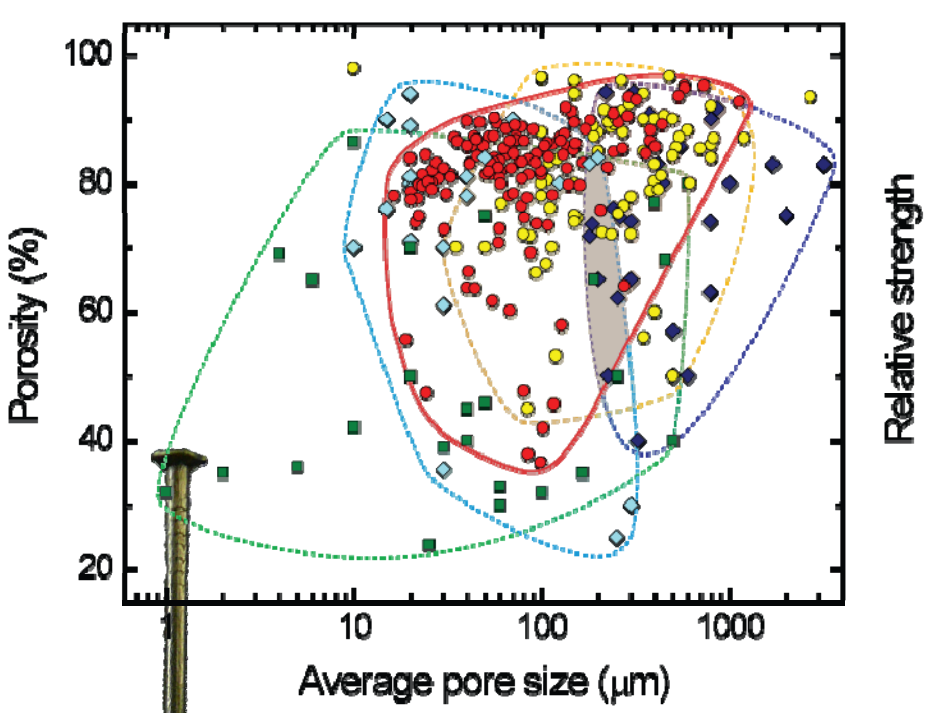
sintering

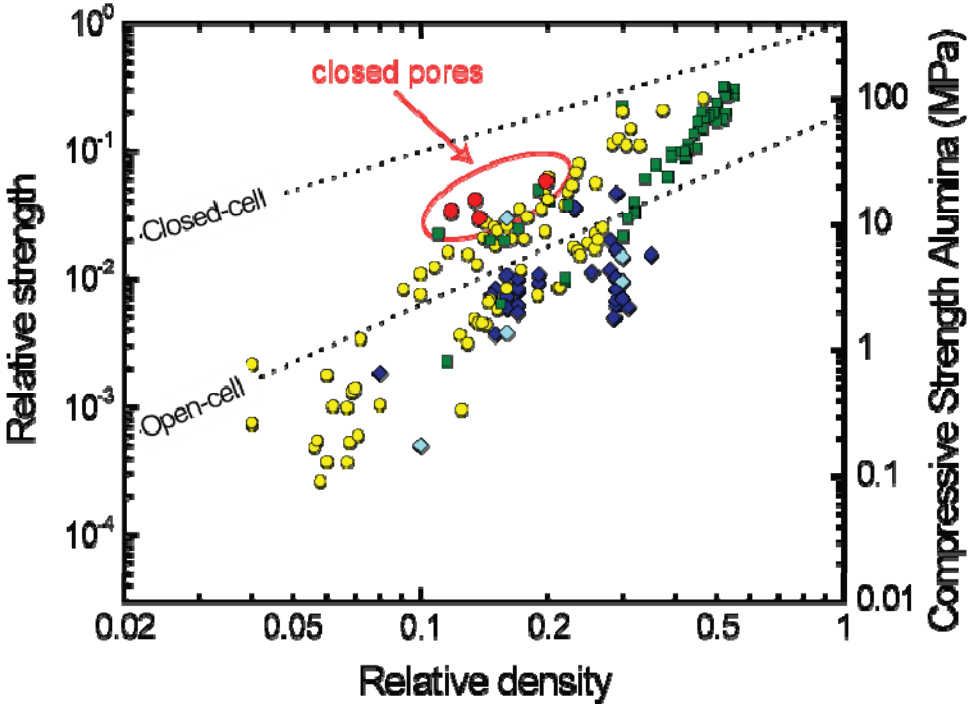

3cm

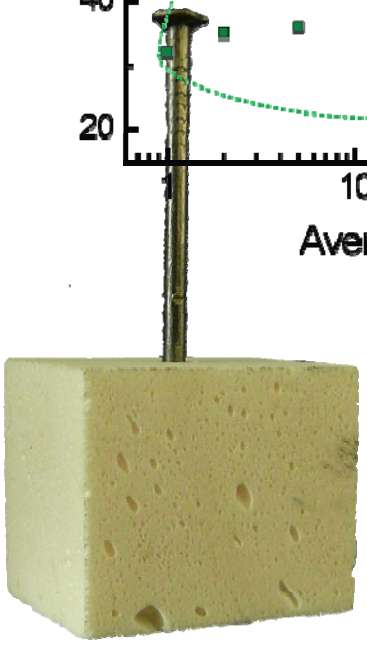

100µm


100µm

PROPERTIES OF POROUS ALUMINA







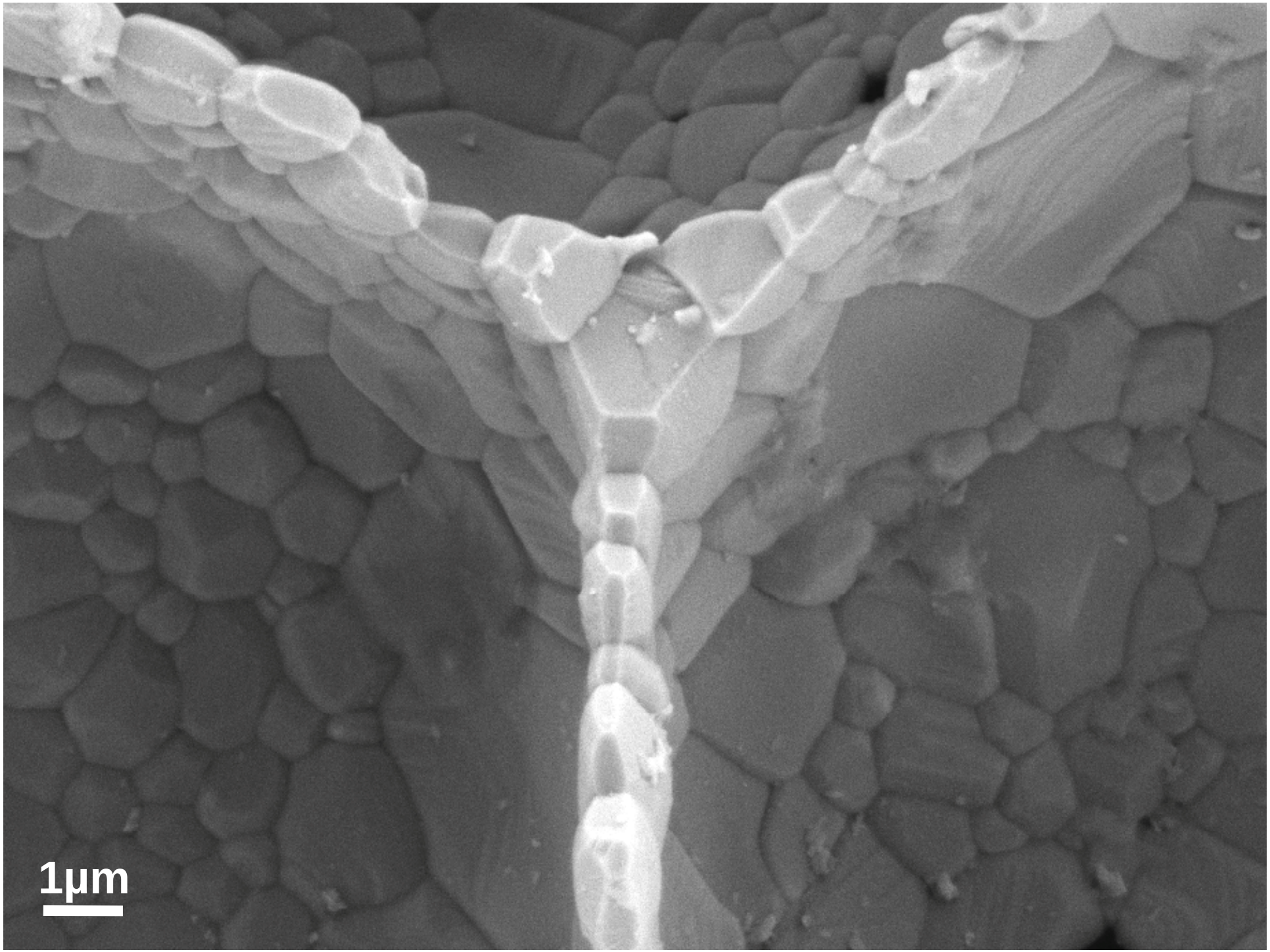
direct foaming with particles

direct foaming with surfactants

polymer replica

wood replica

sacrificial templating


1µm

VERSATILITY OF THE METHOD

Method can be applied to many different materials, e.g.

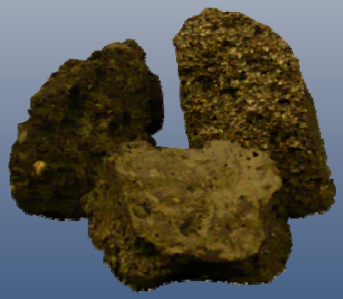
Ceramics

- Al_2O_3
- SiO_2
- ZrO_2
- Ca_3PO_4
- Cements
- ...

1cm

Metals

- Ti
- Al
- Ni/Ti
- ...



1cm

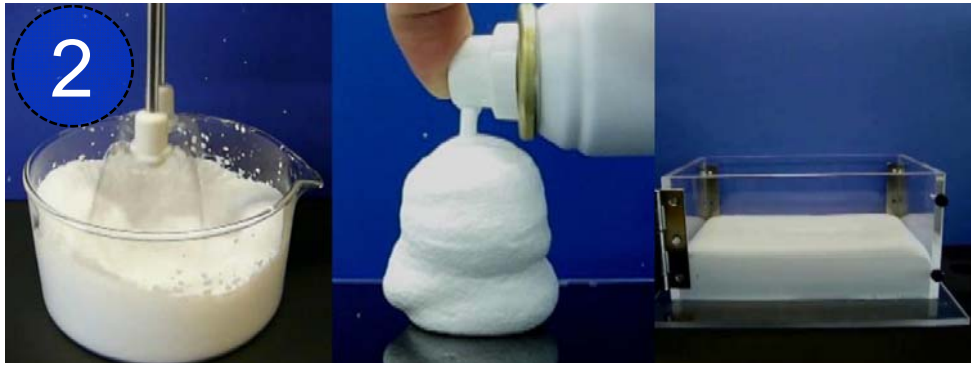
Polymers

- PVDF
- PTFE
- PE
- PP
- ...

1cm

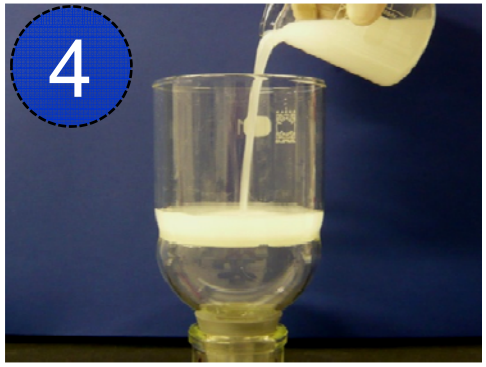
CAPSULE PROCESSING

suspension preparation



foaming

dilution



filtration

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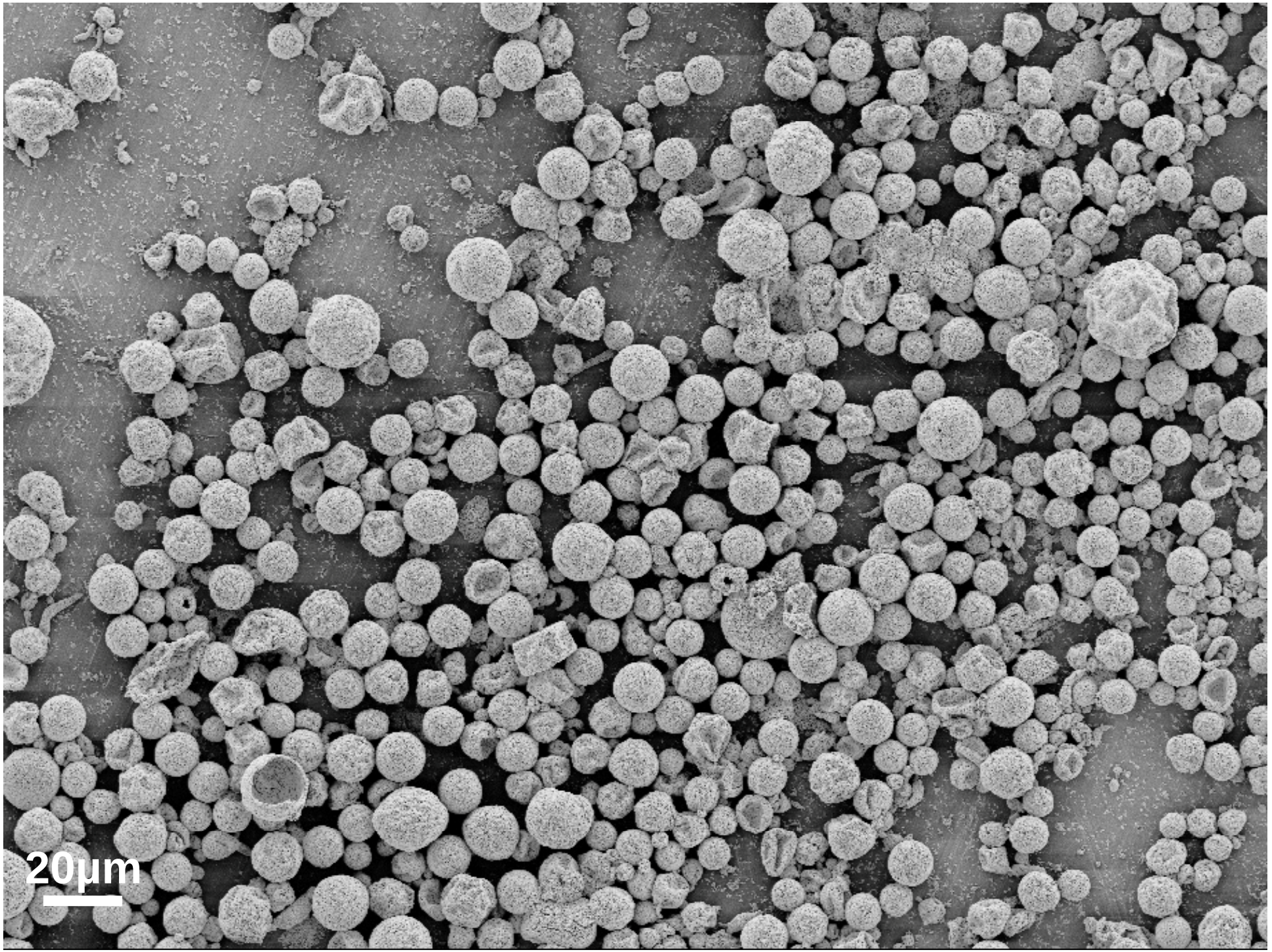
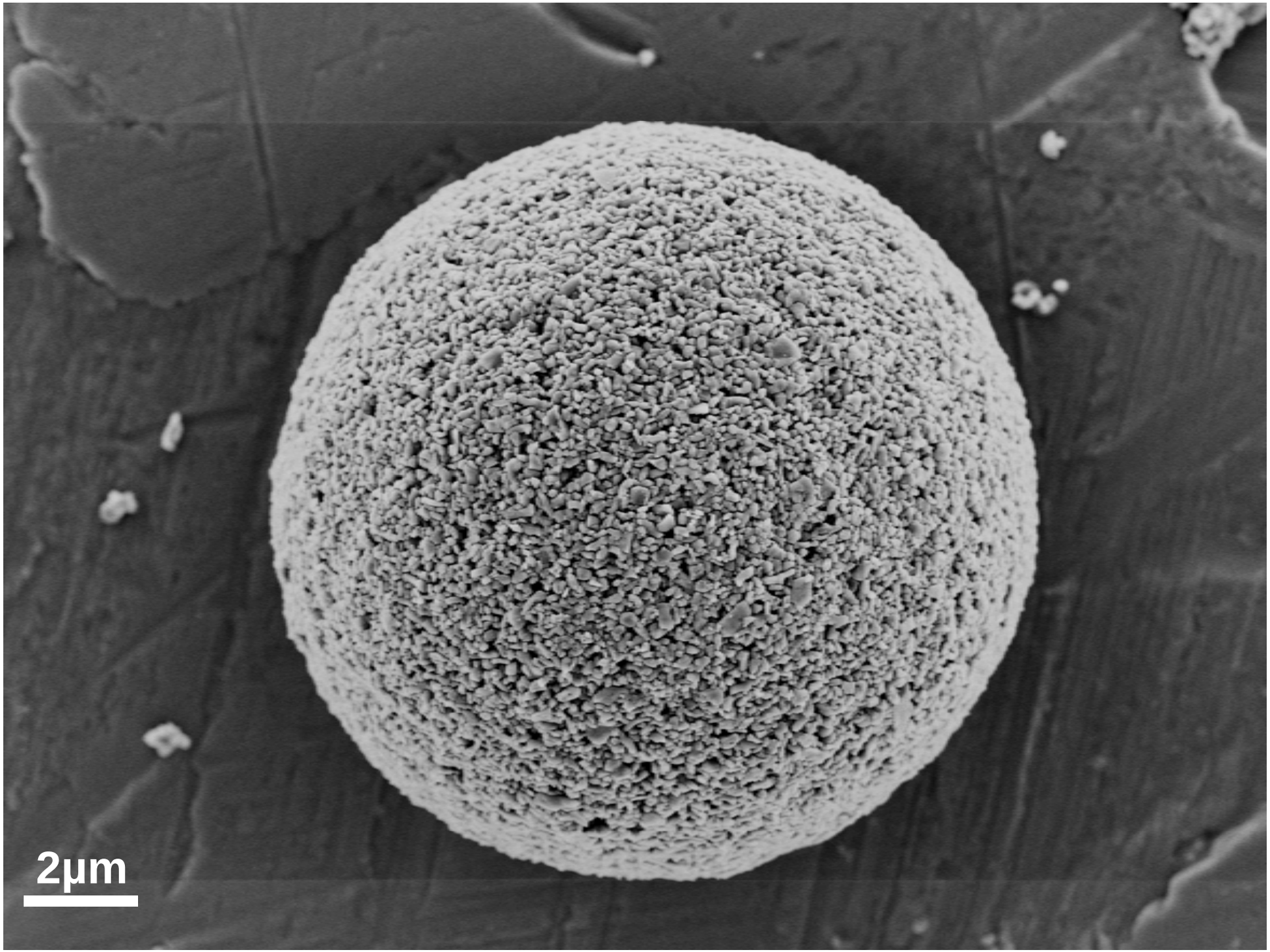
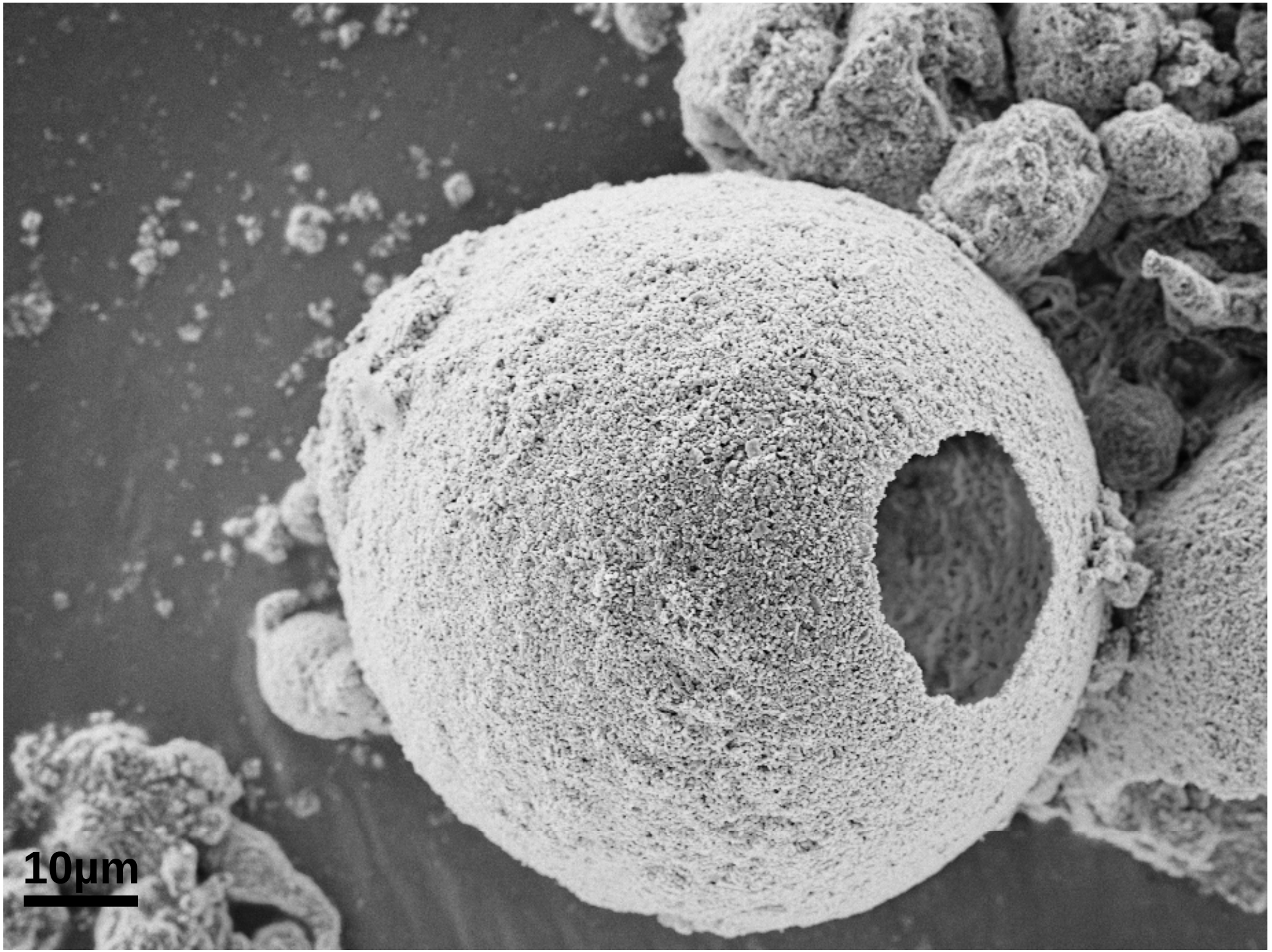
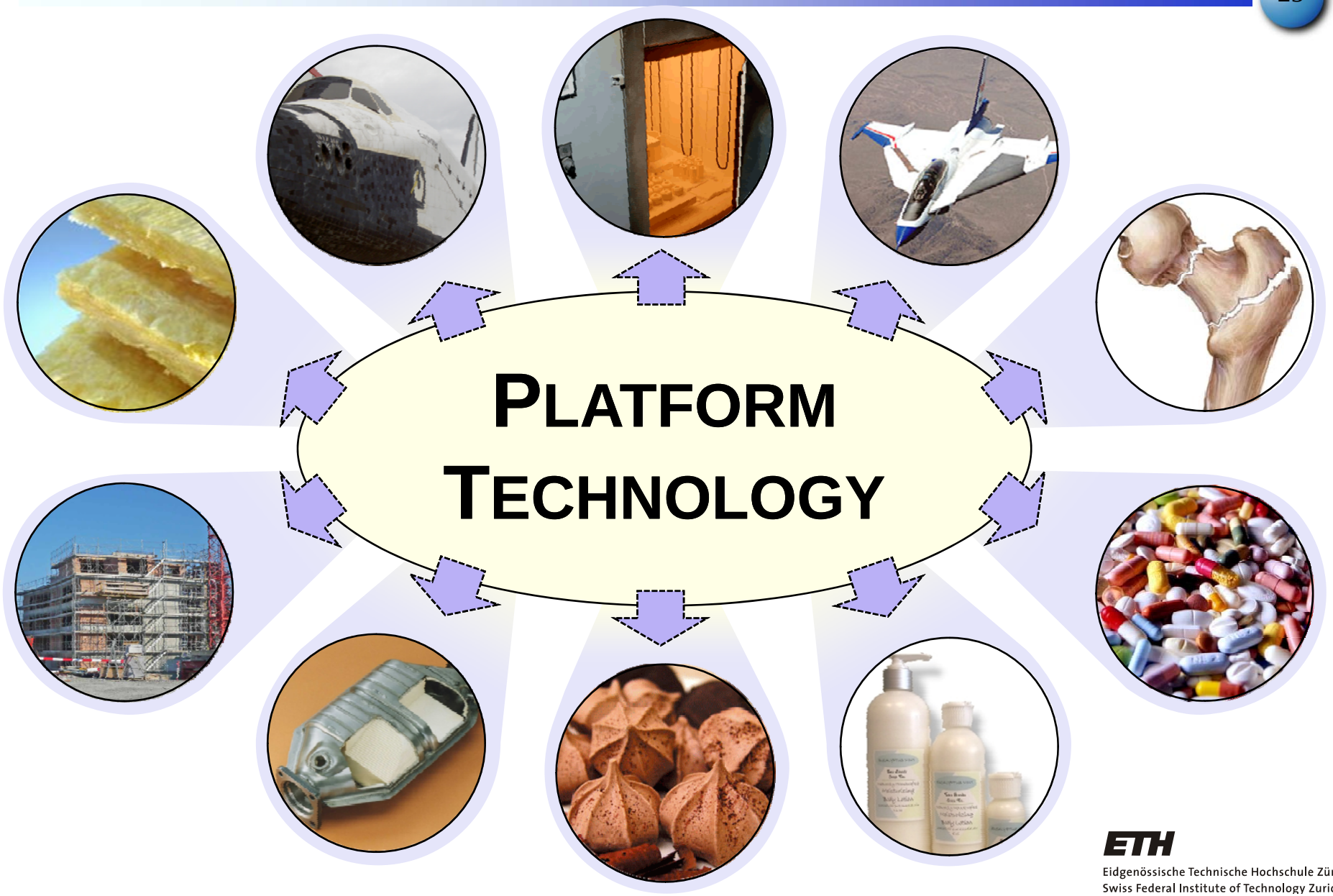

20µm


2µm

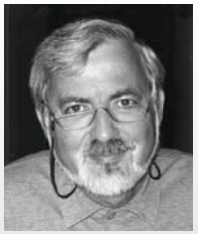

10µm

POTENTIAL APPLICATIONS

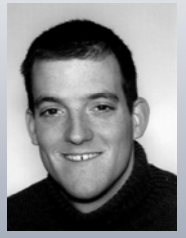


FOAMS AND EMULSIONS AT ETHZ

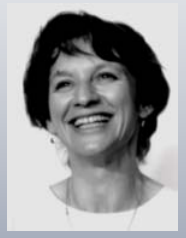
Ceramic foams



Ludwig J. Gauckler



Urs T. Gonzenbach



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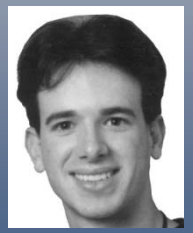


Philip N. Sturzenegger

Ben Seeber

Nonmetallic Inorganic Materials

Metallic foams

Jörg F. Löffler

Florian Dalla Torre

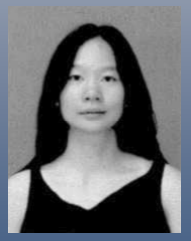
Adrienne Nelson

Laboratory of Metal Physics and Technology

Polymeric foams

Paolo Ermanni

Stephan Busato



Joanna Wong

Center of Structure Technology

Speru

CCMX Competence Centre for Materials Science and Technology

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Thank you!
1cm