Templated synthesis and colloidal processing of porous materials

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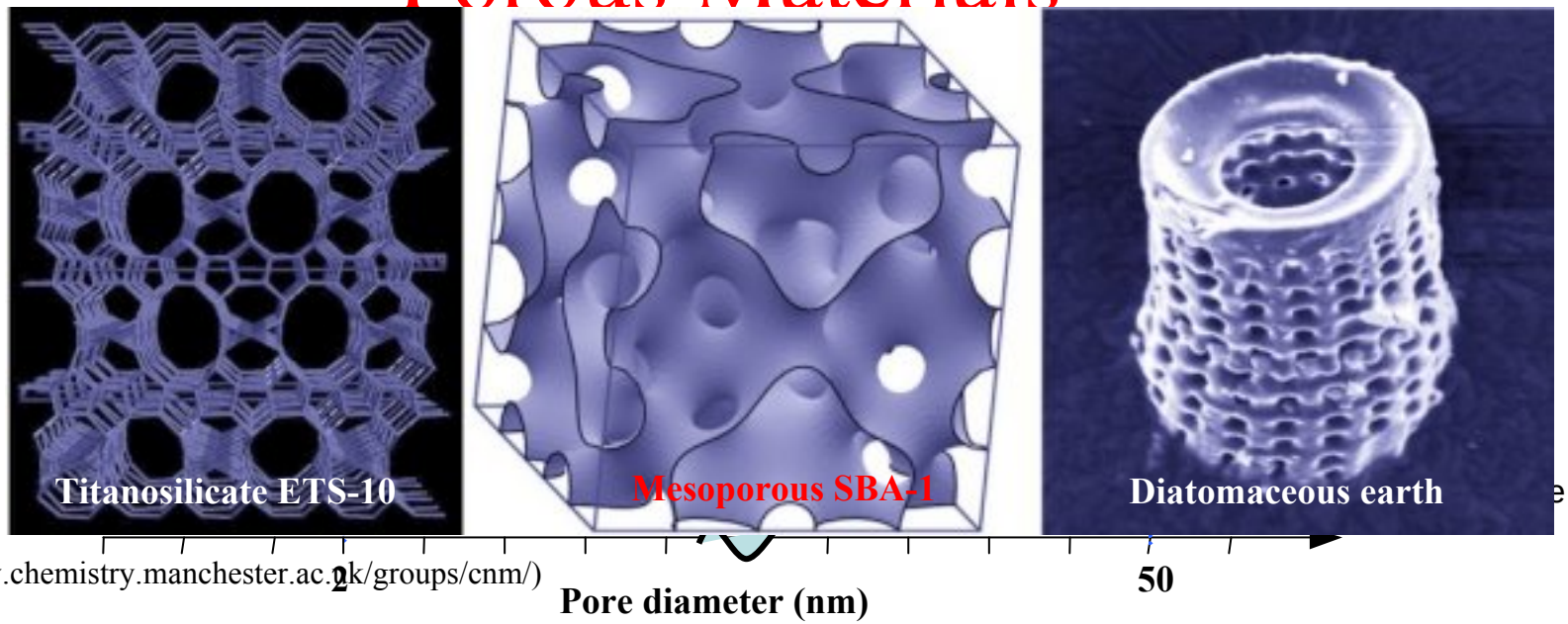
Outline

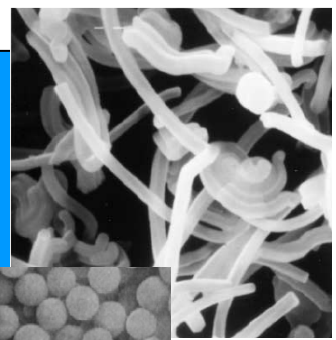
- Introduction
- Mesoporous spheres: synthesis and functionalisation
- Release and transport in mesoporous spheres
- Hierachically porous monoliths
- Novel route to macroporosity
- Summary

Background:
Porous Materials



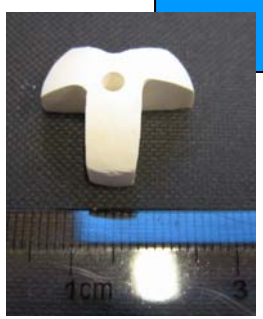
(http://www.chemistry.manchester.ac.uk/groups/cnm/)

(Rathousky et al, Collect Czech Chem Comm 1998)



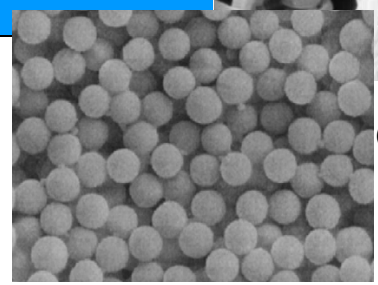
HIGH SURFACE AREA + HIGH ACCESSIBILITY

- **Optimal transport of fluids and gases (pore size range)**
- **High reactivity with size selectivity**



(Vasiliev et al, Chem Mater, 2006)

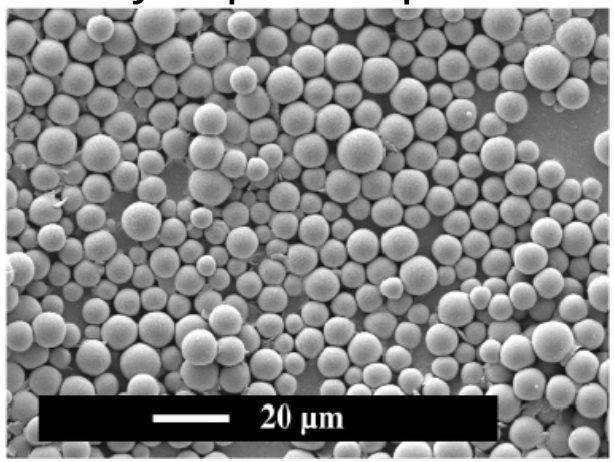
Films **Particles** **Monoliths**



(Ng et al, Micro & Meso, 2008)

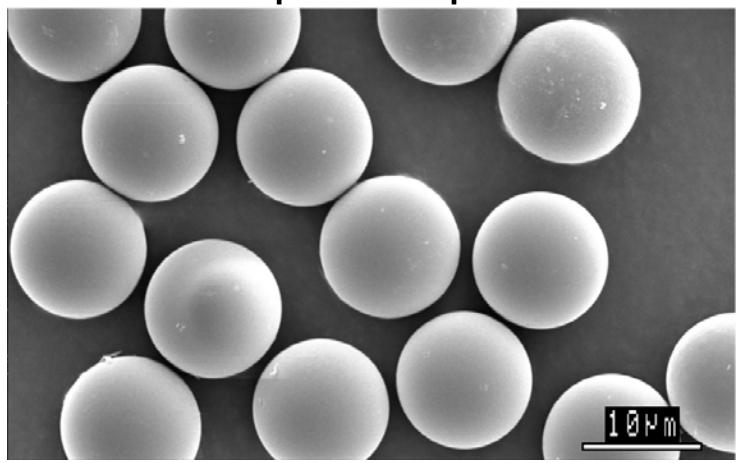
Mesoporous silica particles

Polydisperse spheres



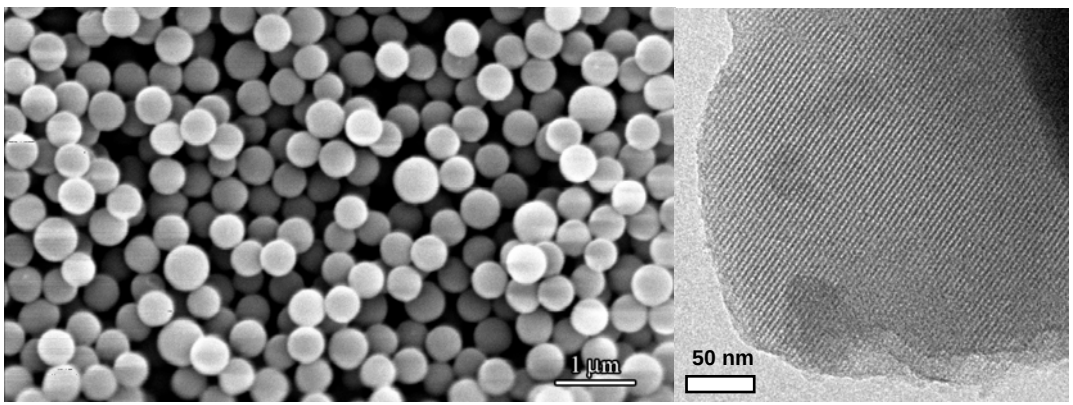
N. Andersson et al., Langmuir, 23 (2007)
Micro Mesoporous Mater., 72, 175 (2004)

Monodisperse spheres



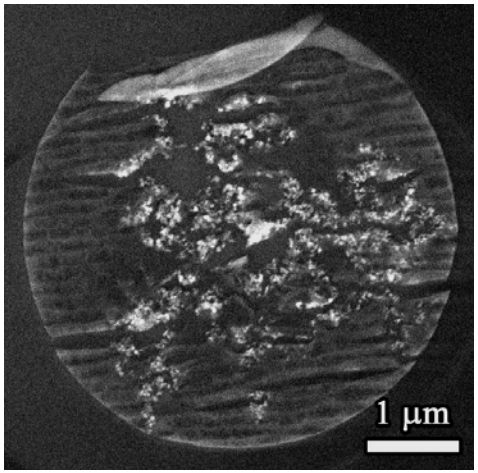
P.O. Vasiliev et al., Chem. Mater., 18 (2006)

Monodisperse MP colloids

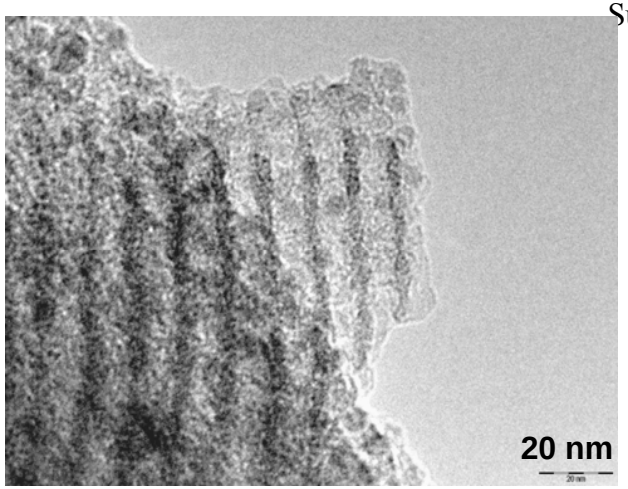


B. S. Ng et al, Micro. Mesoporous Mater., 112 (2008)

Easy to functionalize

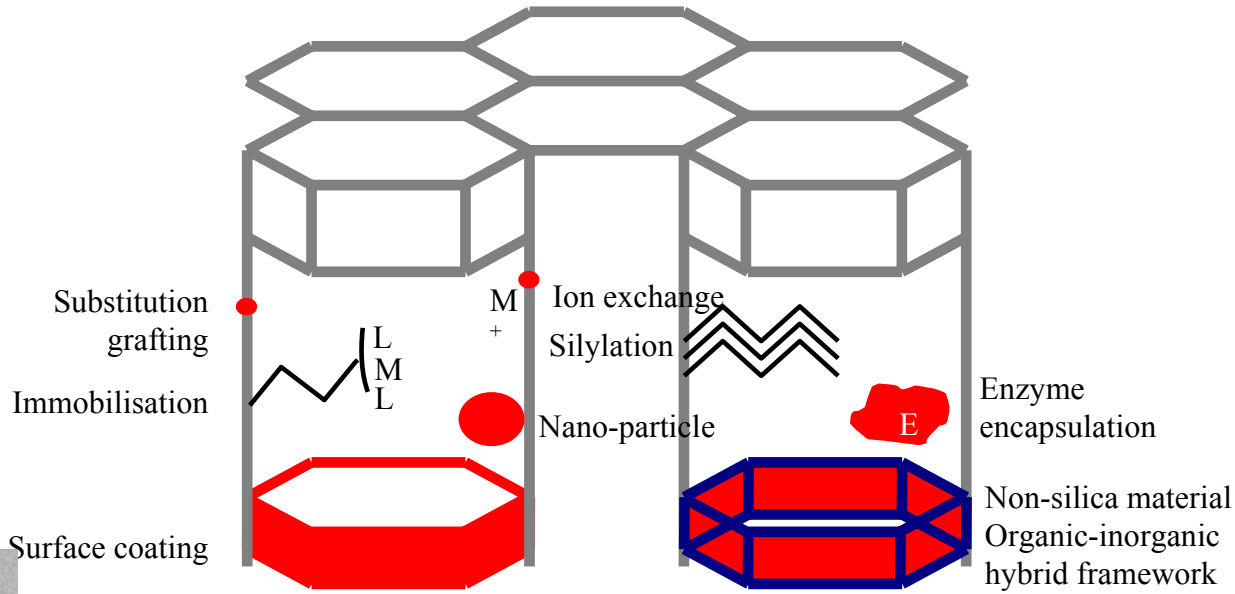


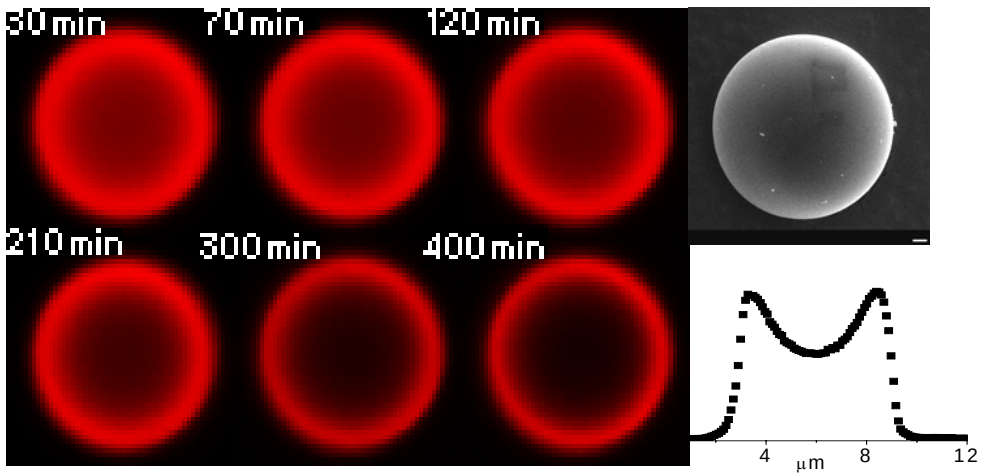
(Vasiliev et al., J. Coll. Interface Sci., 2008)



(Hodgkins et al., Langmuir, 2007)

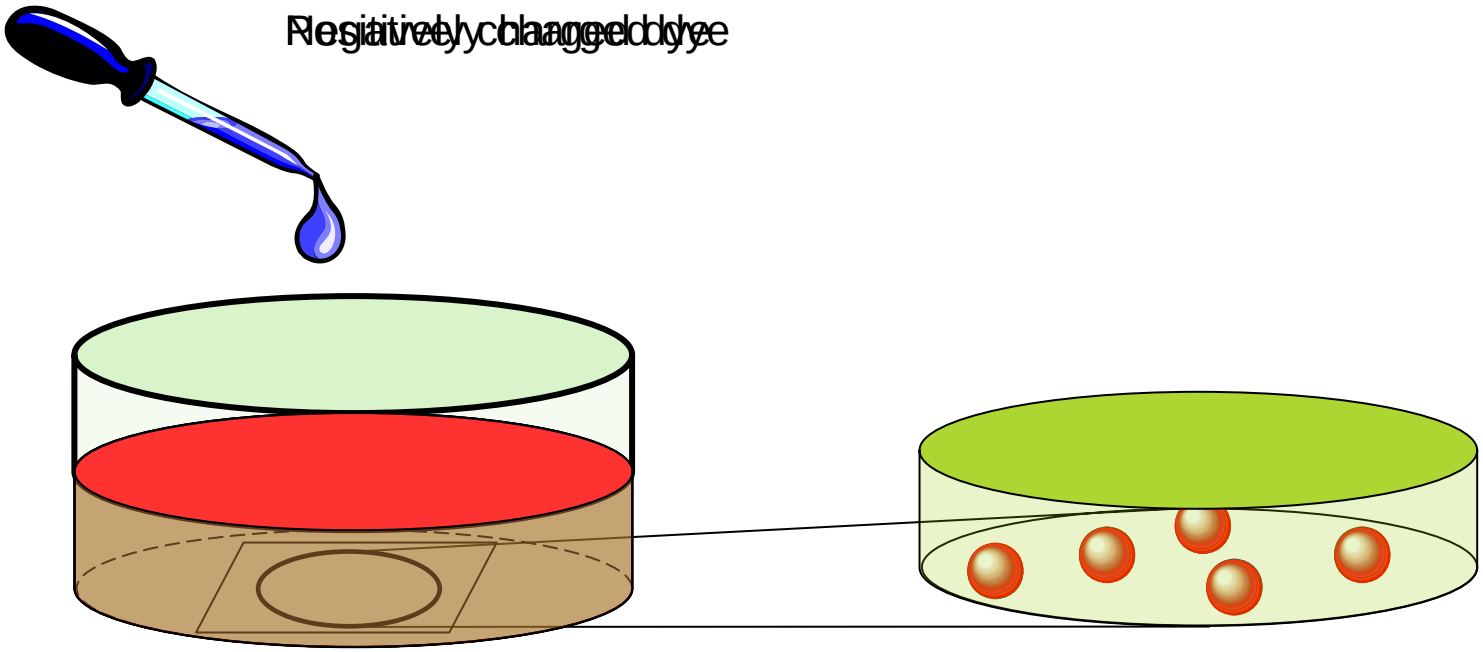
In situ functionalisation or Post synthesis

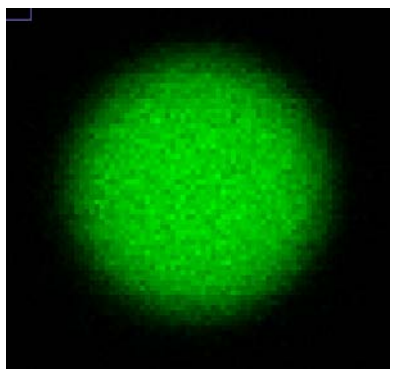


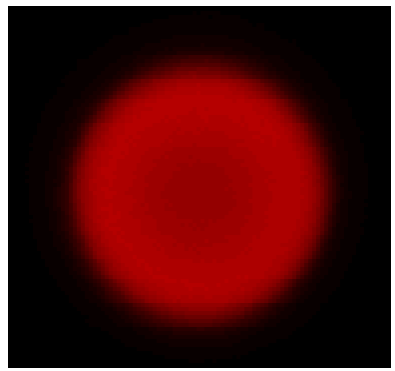


(Ng et al., Langmuir, in press)

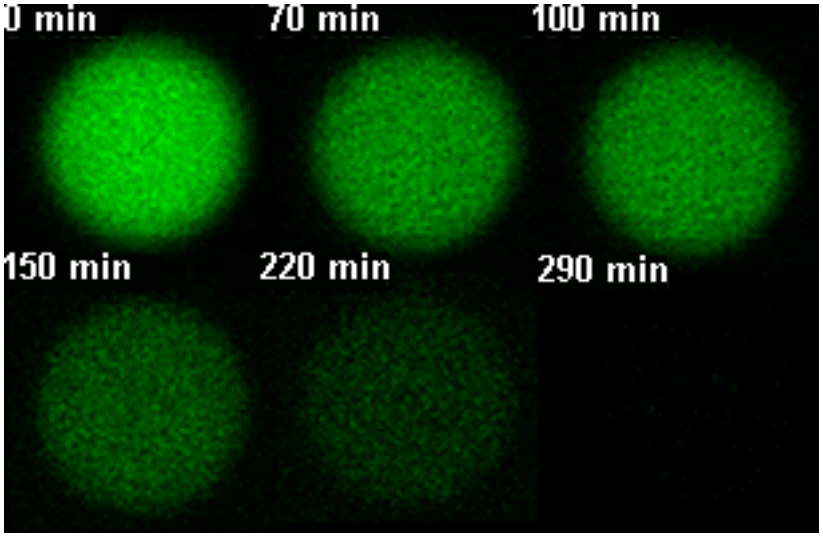
Loading of fluorescent molecules

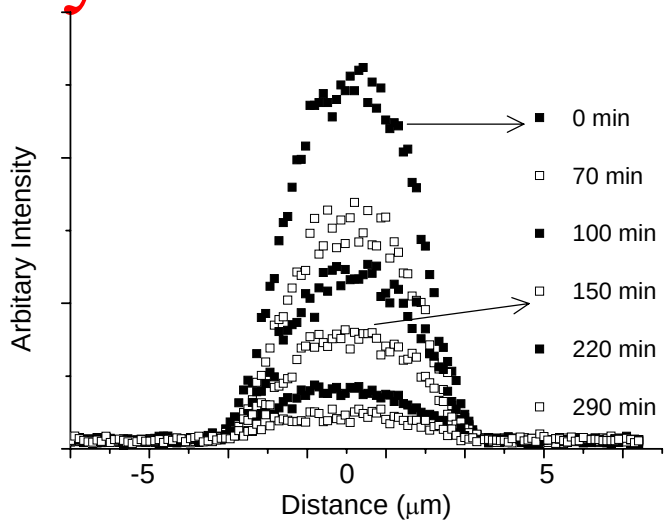


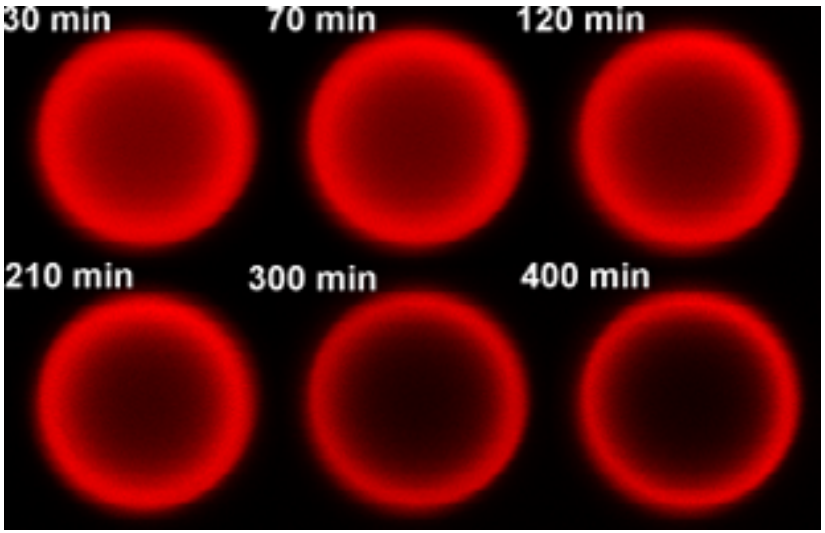


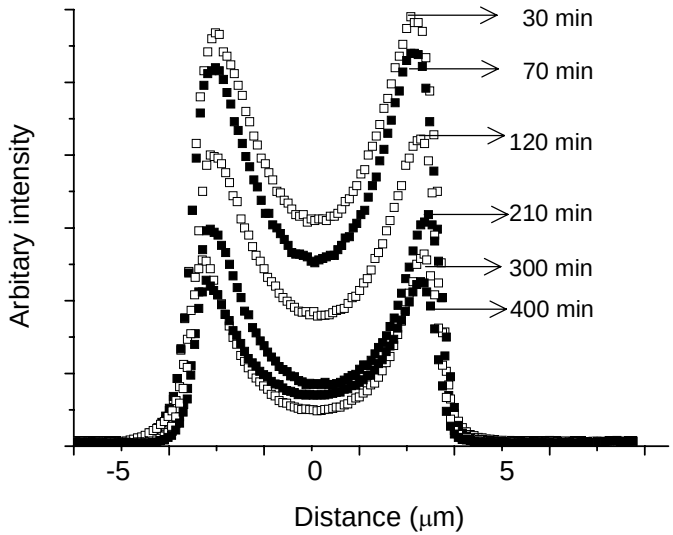


Release of cationic and anionic dyes







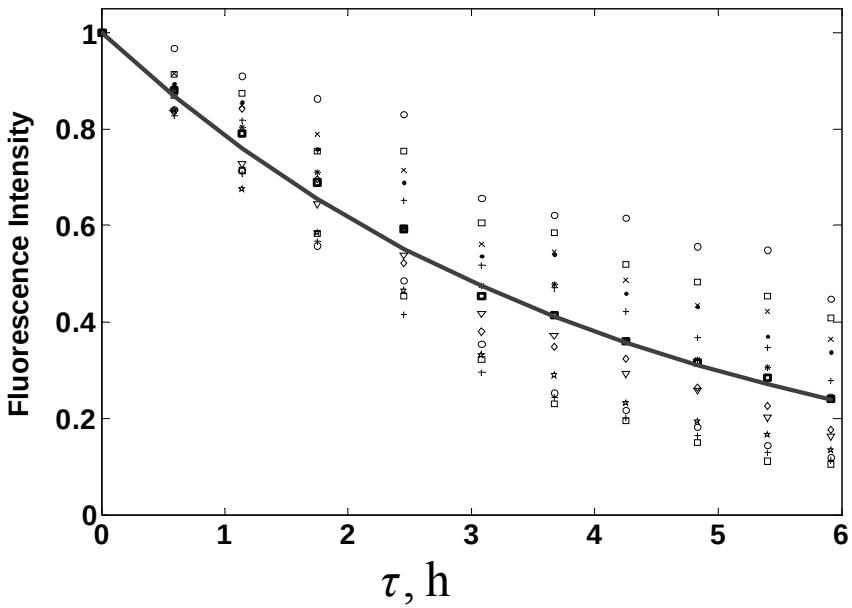


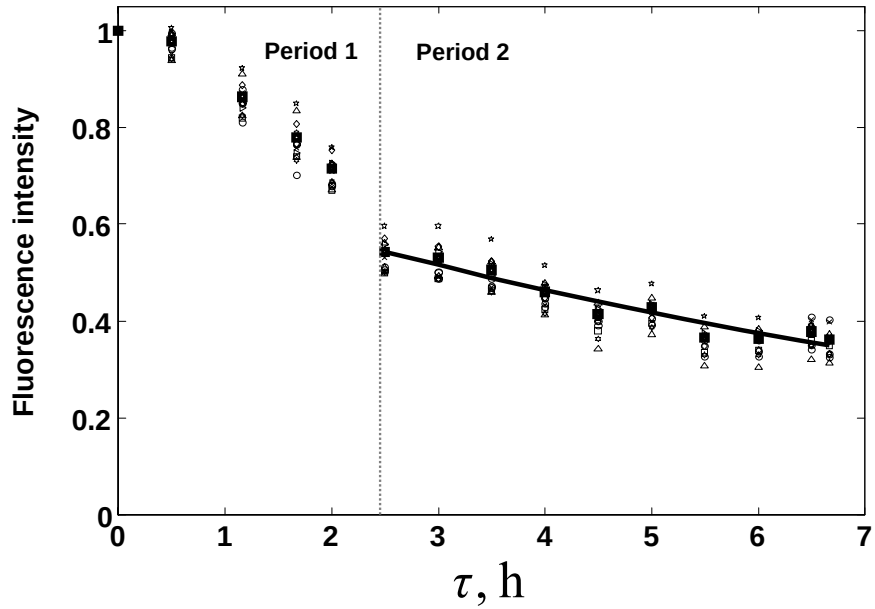
Bulk release

Anionic dye

$$\frac{I_t}{I_0} = \frac{6}{\pi^2}\exp\left(\frac{-\pi^2 Dt}{R^2}\right)$$

Cationic dye





Fickian release:

D_{eff}= 0.62 ± 0.12 x 10^{-12} cm^2s^{-1}

(6 oreders of magnitude lower than the bulk diffusion in Tris EDTA buffer = 1.3 x 10^{-6} cm^2s^{-1})

* Note: 1. The intensity have been normalized for both plots. 2. Bleaching was compensated for the anionic dye.

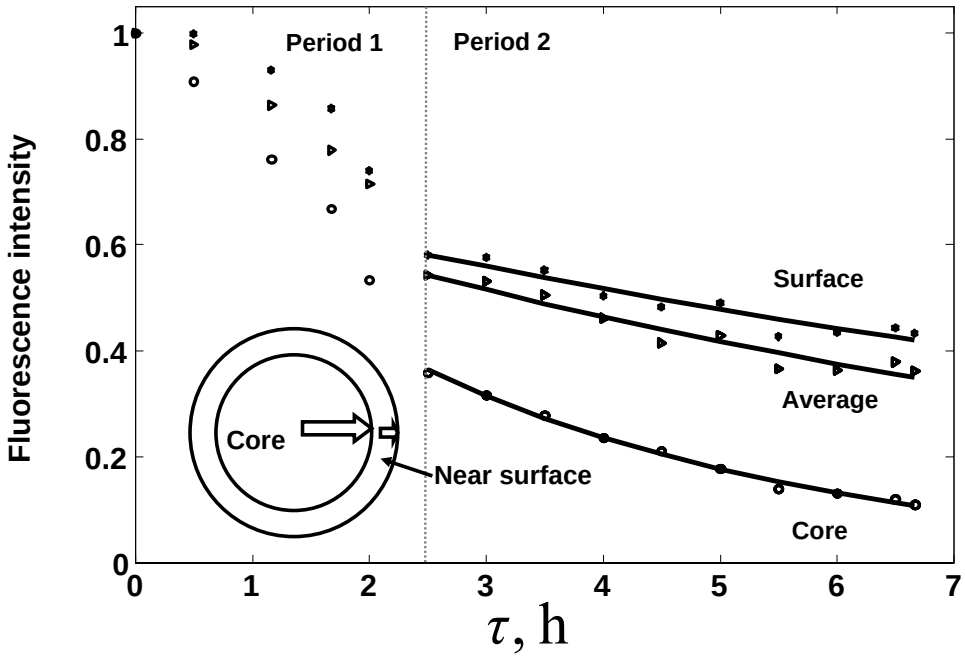
Two-stage release

Later stage Fickian release:

D_{eff} = 0.24 ± 0.04 x 10^{-12} cm^2s^{-1}

(7 orders of magnitude lower than the bulk diffusion coefficient in water = 2.8 x 10^{-6} cm^2s^{-1})

Molecular transport inside the material



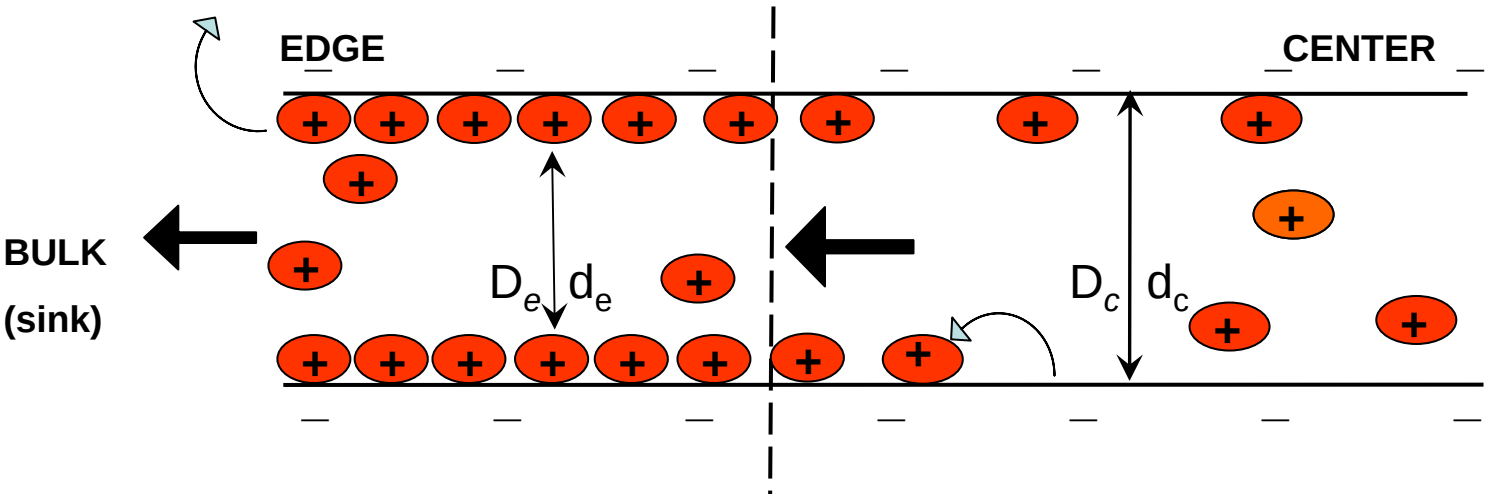
Two-stage release

Later stage Fickian release:

$D_{edge} = 0.2 \times 10^{-12}\ cm^2 s^{-1}$

$D_{center} = 0.73 \times 10^{-12}\ cm^2 s^{-1}$

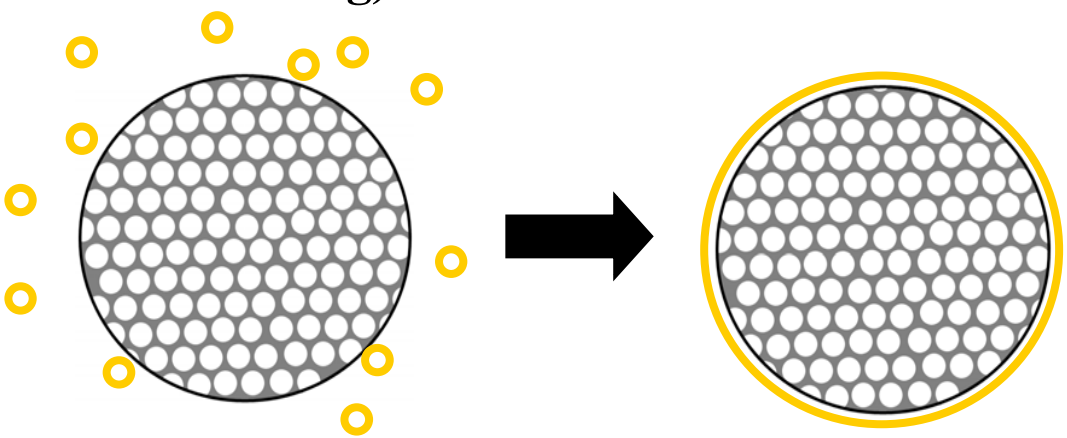
$D_{average} = 0.24 \times 10^{-12}\ cm^2 s^{-1}$

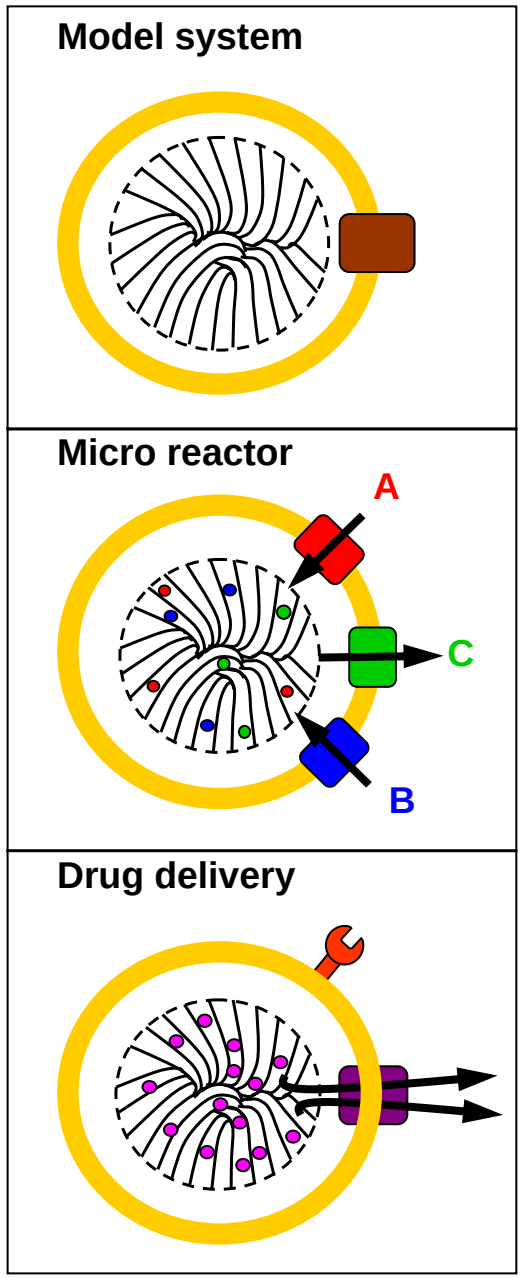


Langmuir, in press

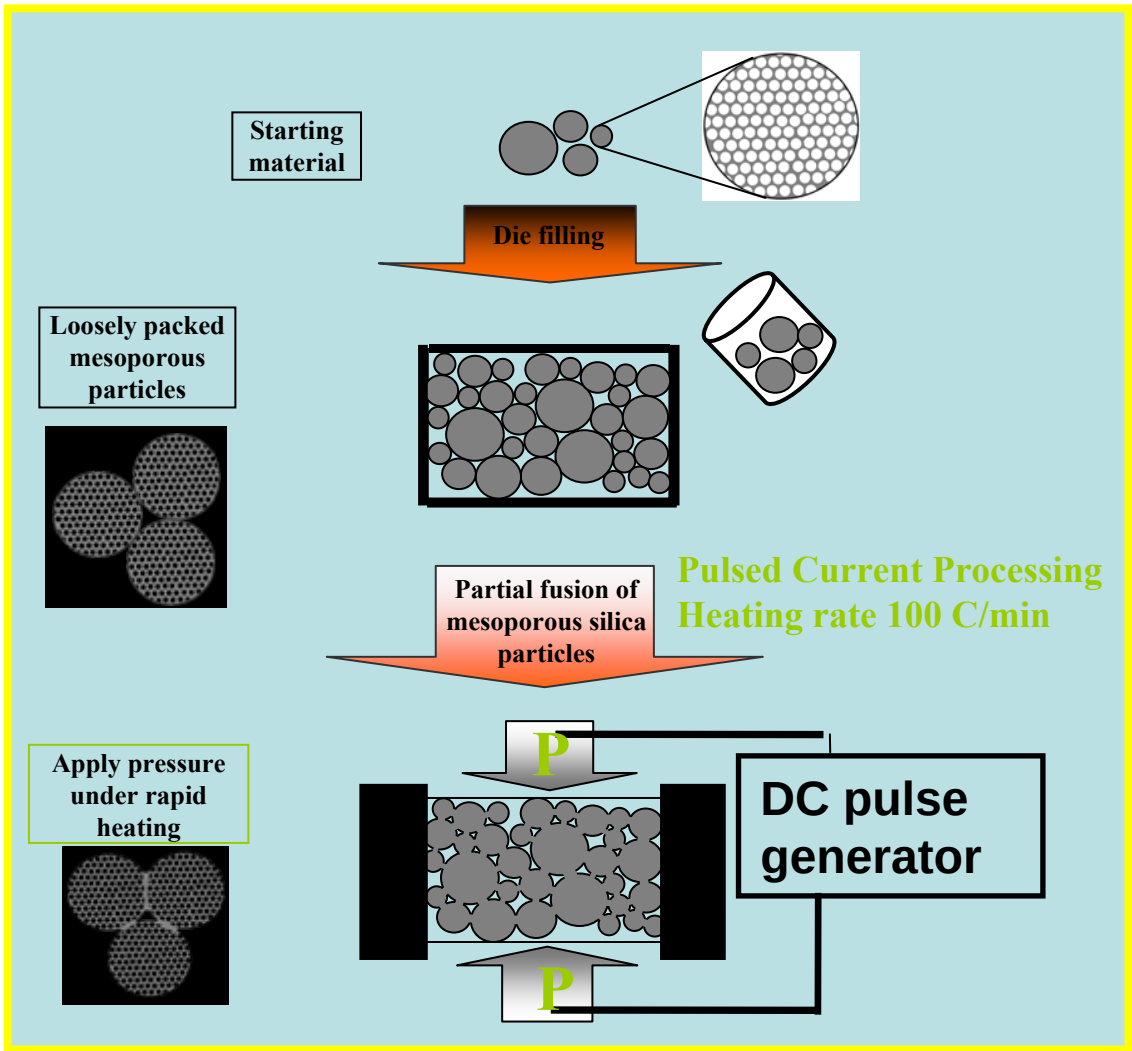
Ongoing work

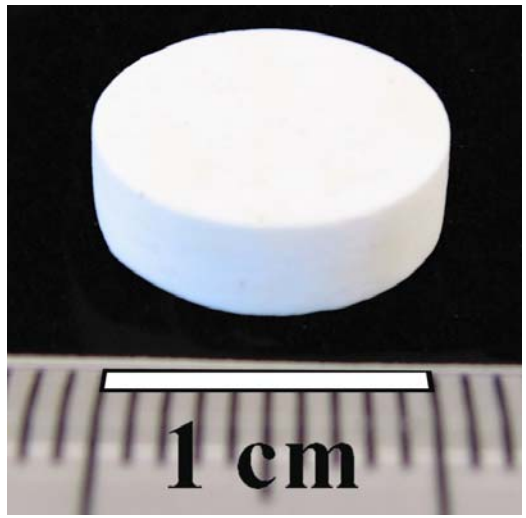
1. **Effect of guest molecule-host mesopore size ratio on the molecular transport kinetics**
2. **Impact of enzyme spatial distribution on enzymatic activity using large pore mesoporous spherical particles as carriers**
3. **Solid support for membrane protein-containing lipid bilayers (biosensing, bioscreening)**

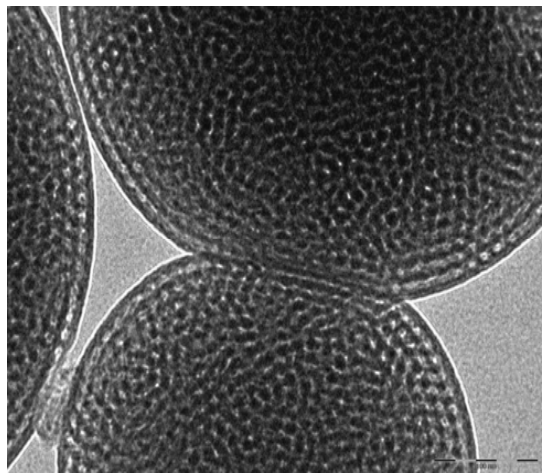




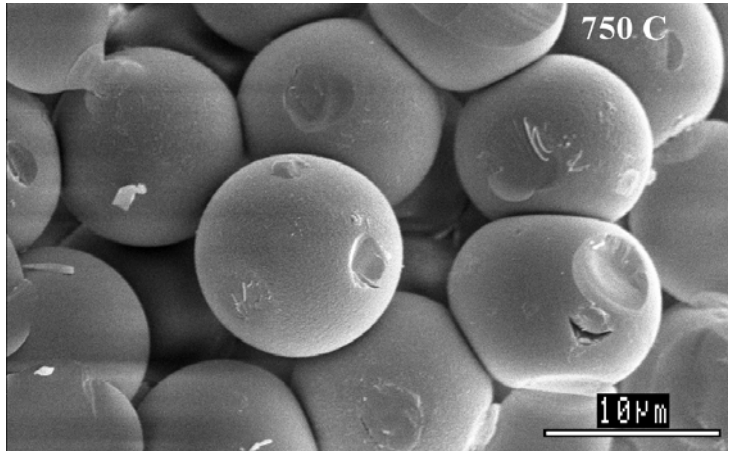
Producing hierarchically porous materials

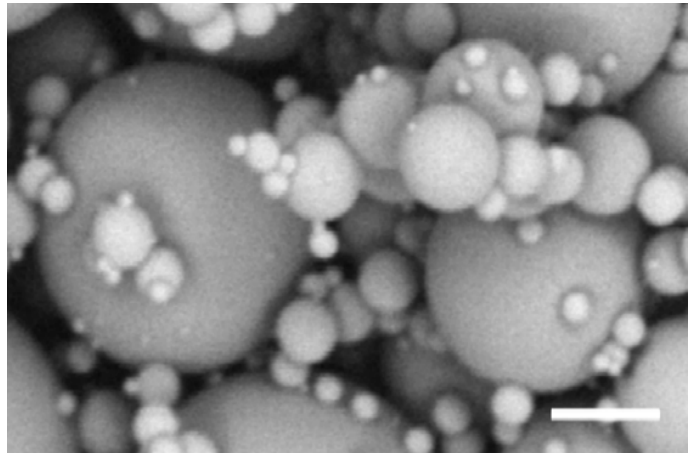


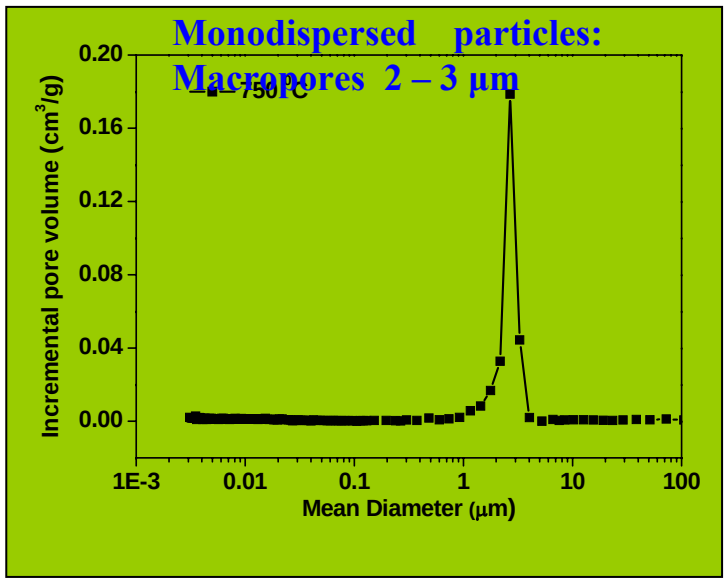


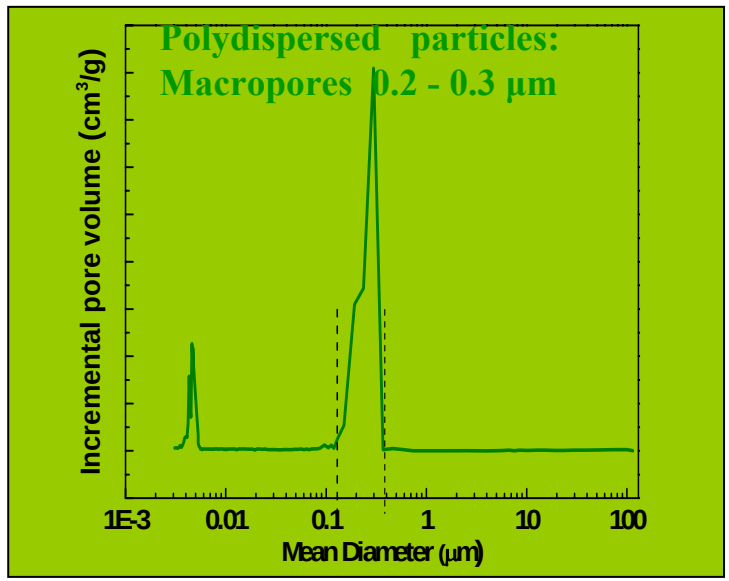


Vasiliev et al., Chem. Mater., 18, 4933 (2006)





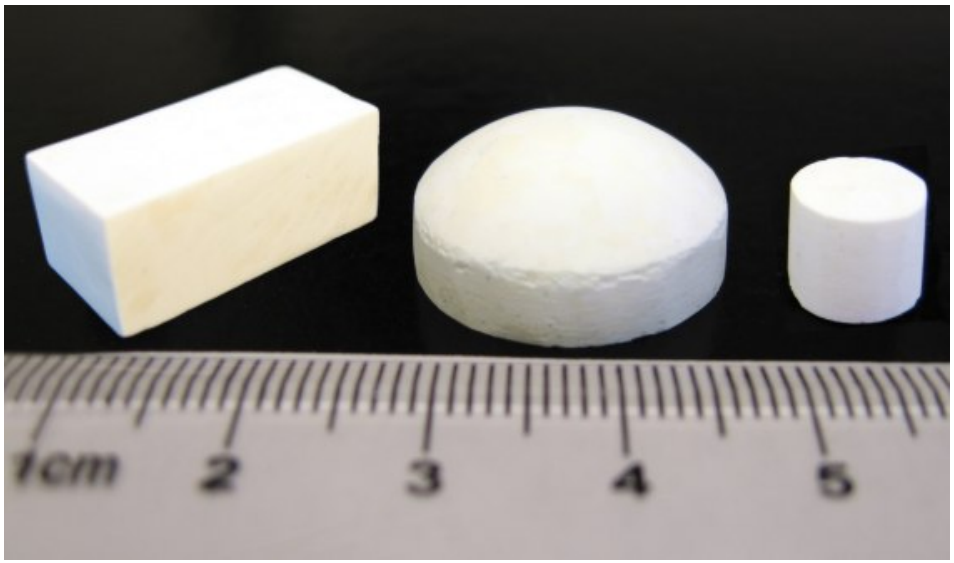


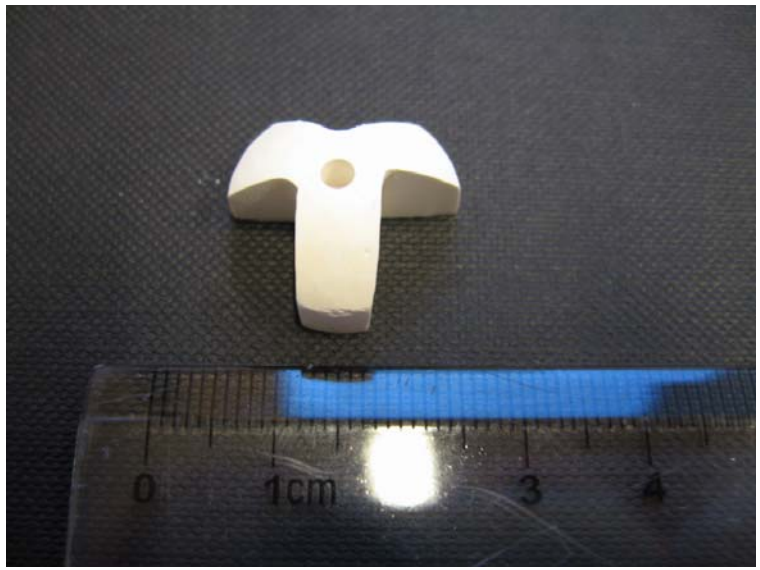


Mercury porosimetry data displaying a macropore size 2-3 µm; mesoporosity (CTAB) - 21 Å.

the macropore size can be tailored depending on the initial average particle size of the as-made mesoporous spheres

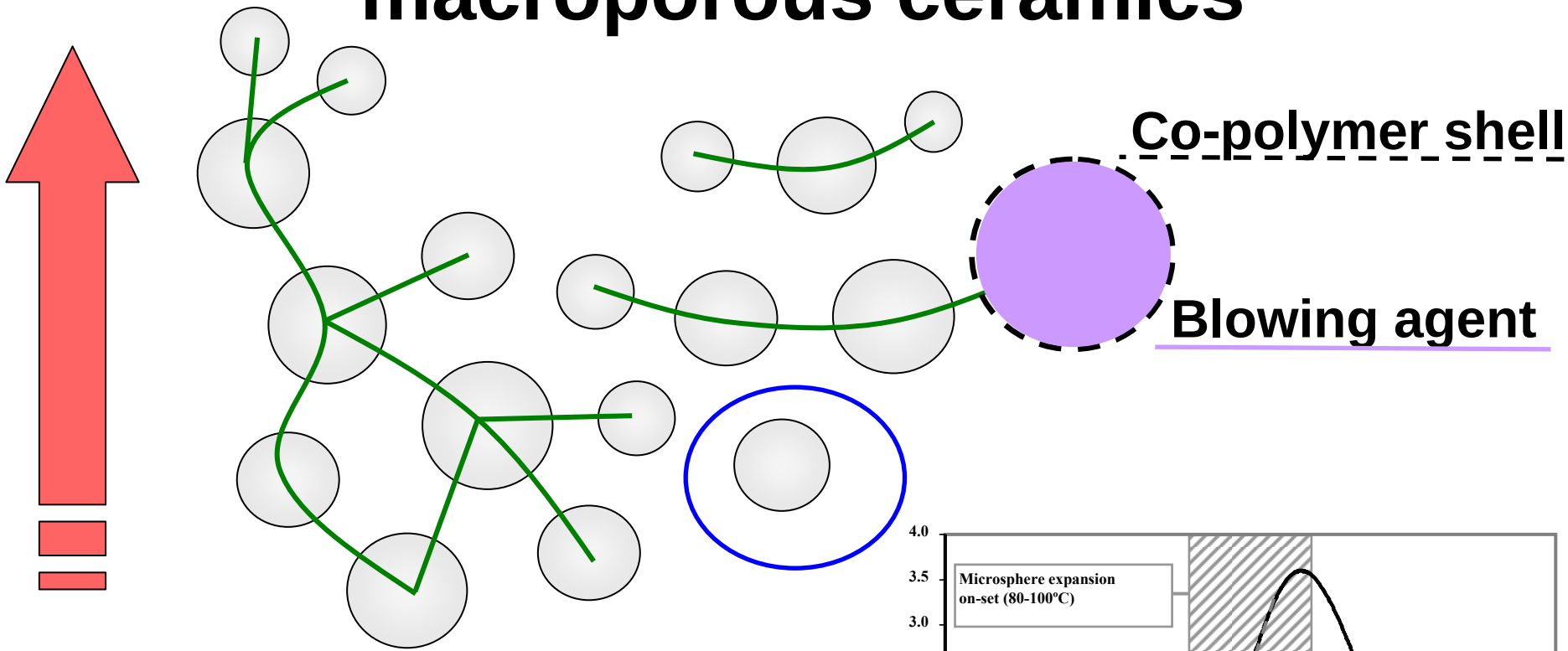
Hierarchically Porous Complex Shaped Monoliths





Mechanically stable, with high surface area, hierarchically porous monolith with complex geometry

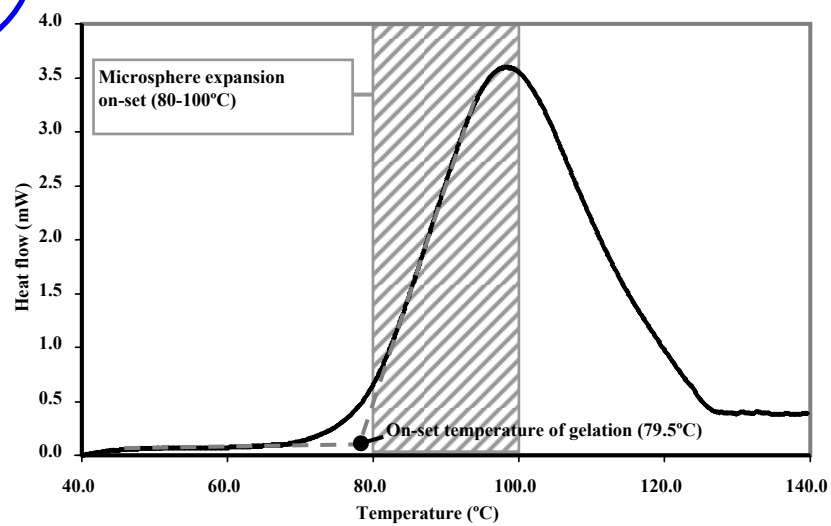
Direct casting of complex shaped macroporous ceramics



Monomer x =

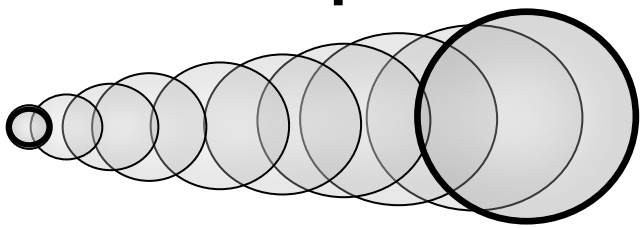
Crosslinker = y =

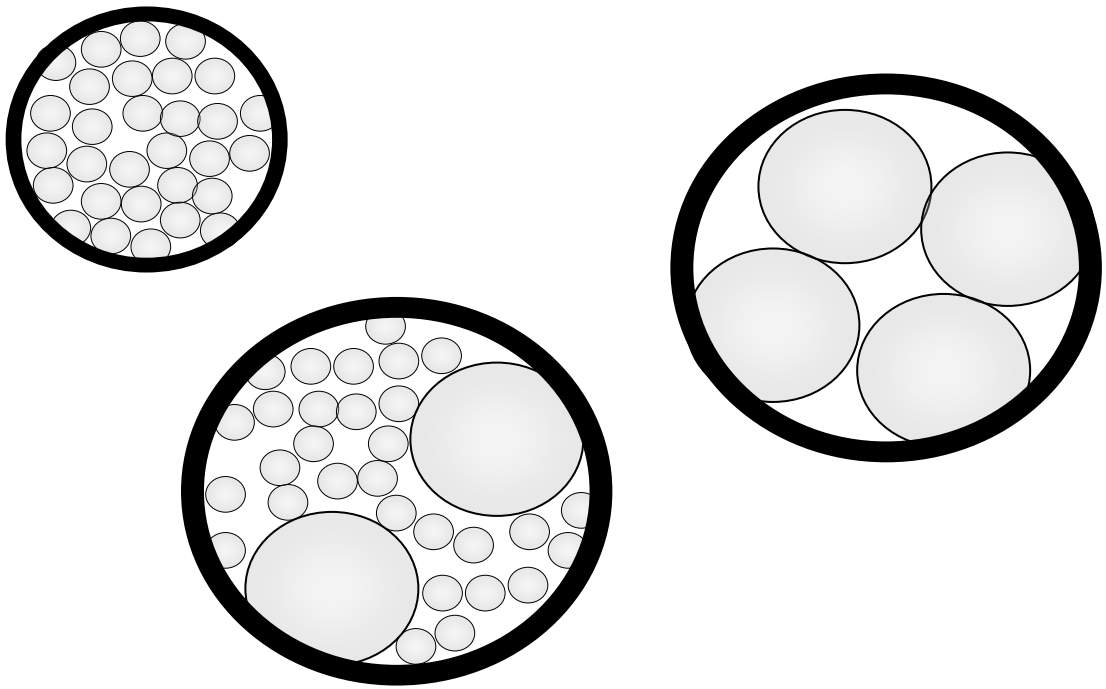
Initiator

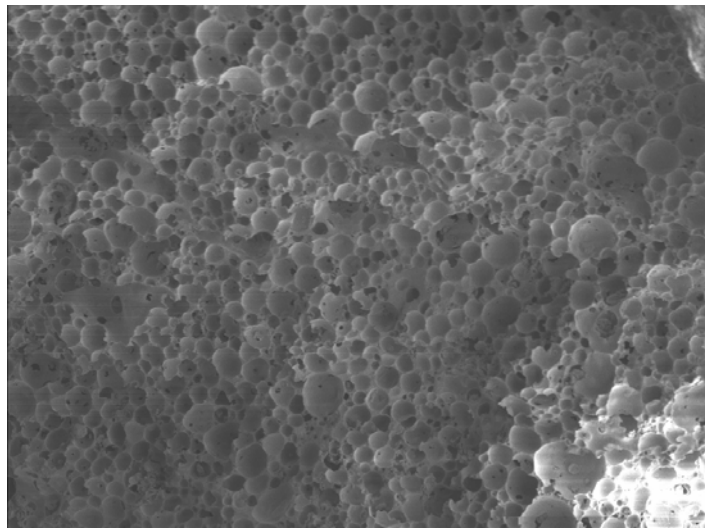


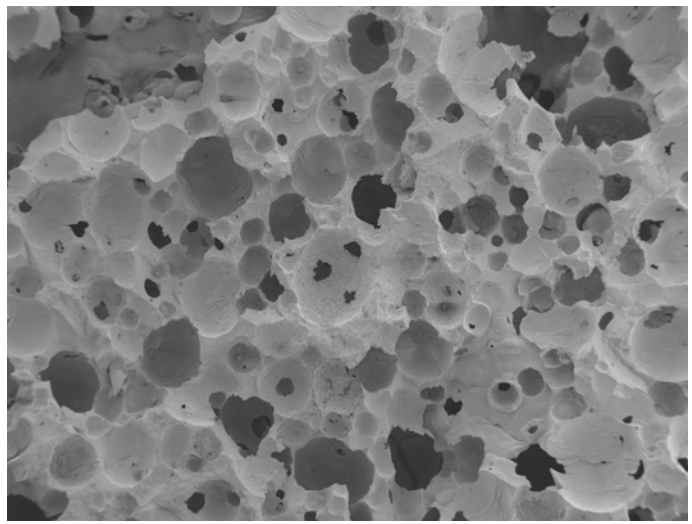
Expandable spheres: tunable pore size and pore volume

Expanded size:
20 – 150 µm





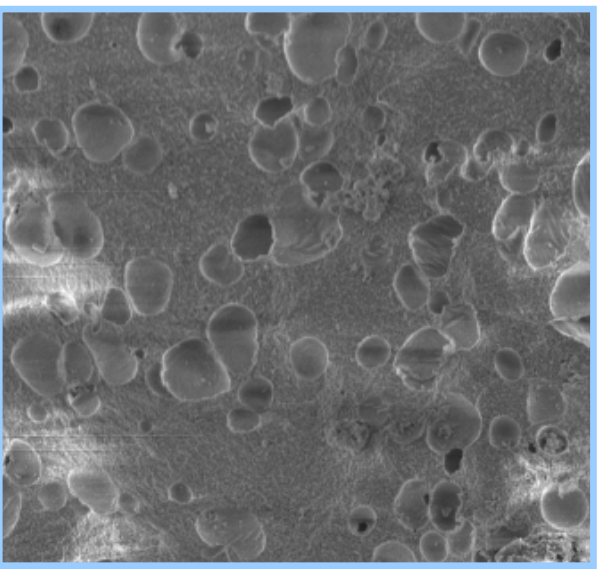




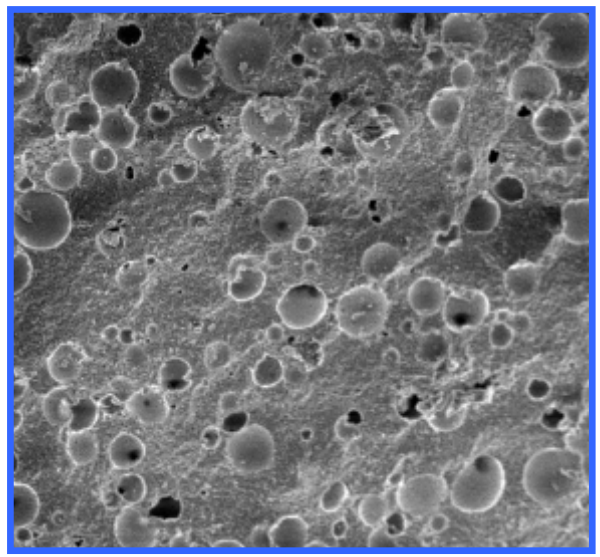
Tailoring the pore volume

40 vol%

4 wt%

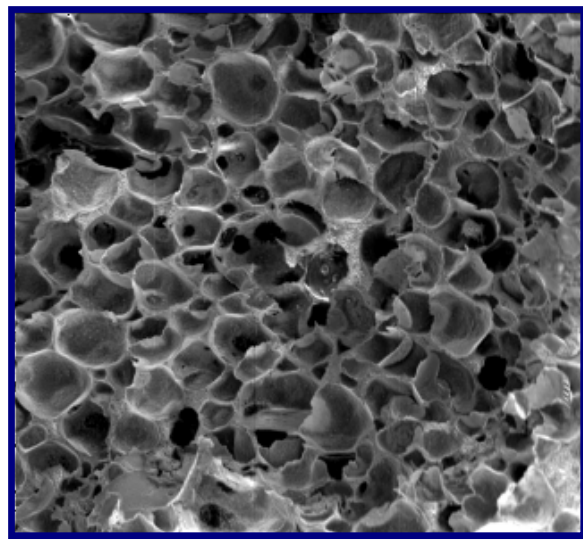


55 vol%

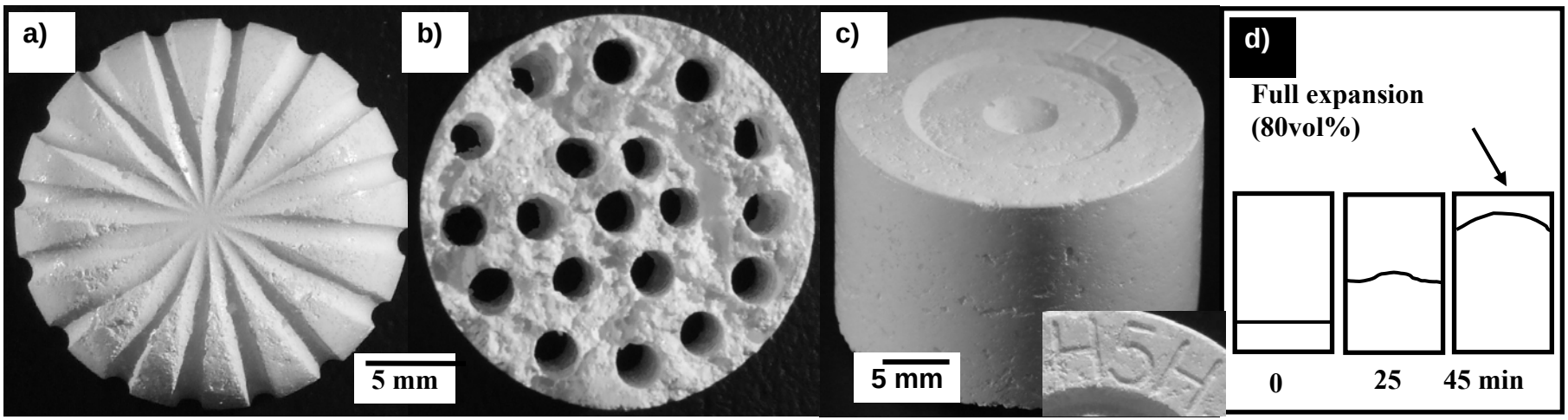


85 vol%

6 wt%

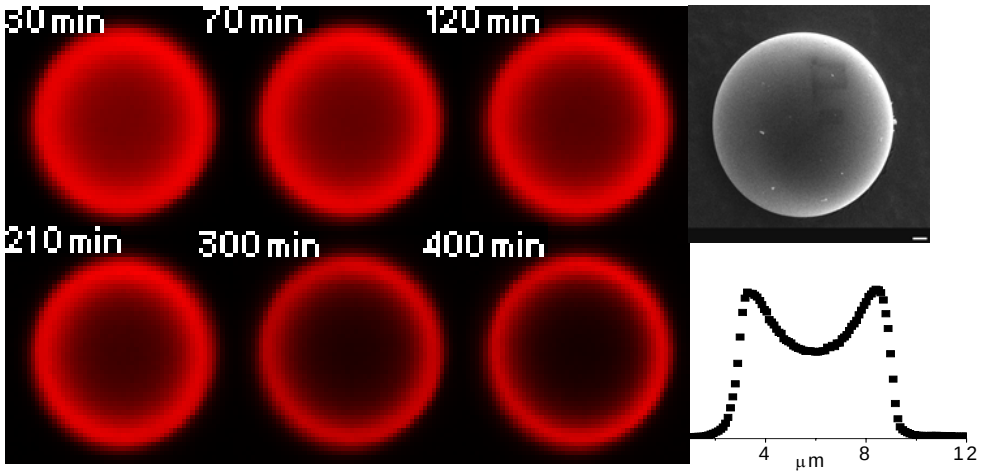


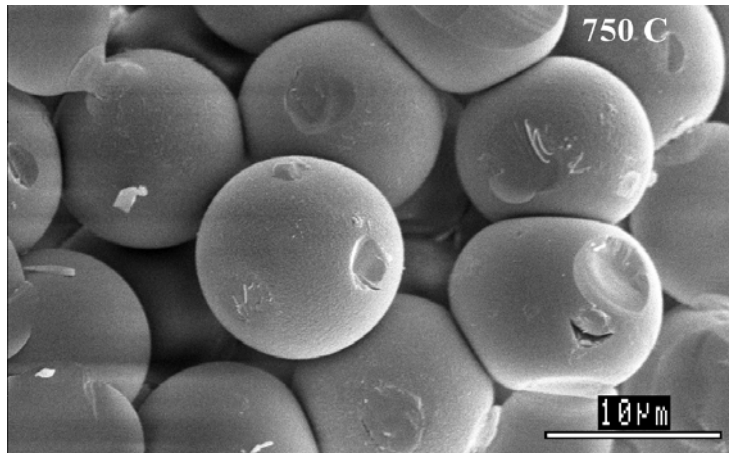
Zero-pressure injection moulding

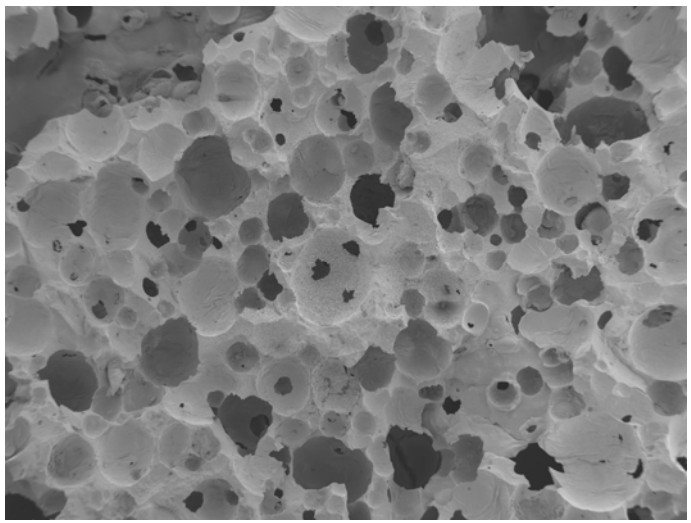


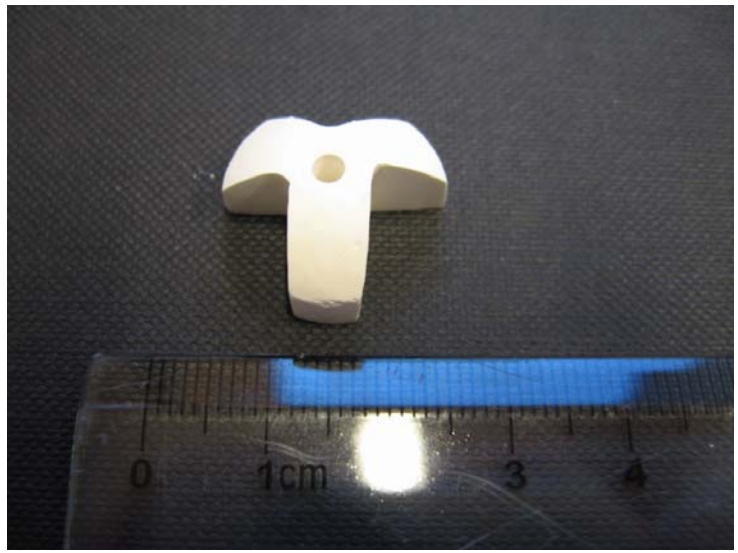
L. Andersson, L. Bergström, J. Europ. Ceram Soc.,28, 2815-2821 (2008)

Summary


30 min
70 min
120 min
210 min
300 min
400 min
4
μm
8
12


750 C
10μm




0
1cm
3
4

Acknowledgements

Stockholm University: Anwar Ahniyaz, Farid Akhtar
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