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**Sol-gel process and complex fluids:  
sculpting porous matter at various lengths scales toward  
the Si(HIPE), Si(PHIPE) and SBA15-Si(HIPE) series**

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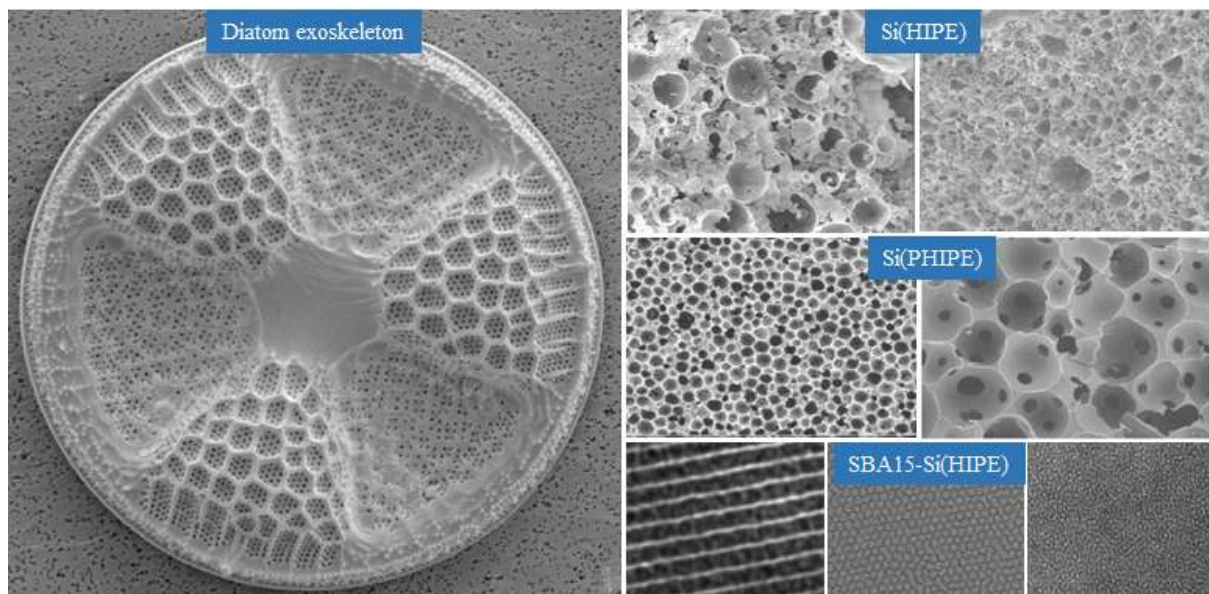
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**Abstract**

Taking inspiration from diatom hierarchically organized porosity, synthetic porous monoliths have been synthesized through rational designs while combining sol-gel chemistry, emulsions, Pickering-based emulsions and lyotropic mesophases. We have described the synthesis of the Si(HIPE) series employing traditional emulsions to tune the macroscopic void diameters and cationic surfactant molecules to both stabilize the oil/water interface at the macroscopic length scale and create vermicular poorly organized porosity at the mesoscopic length scale. In a second part, while substituting surfactant molecules with modified silica nanoparticles acting as emulsion-stabilizers, we depict the possibility of tuning independently the macroscopic cell diameters and the cell junctions *via* Pickering emulsions employed as templates, leading to the Si(PHIPE) series presenting both monodisperse macroscopic void and cell junction diameters. Finally taking the synergetic effect of nonionic surfactants and a kosmotrope salt effect we show that it is possible generating self-standing Si(HIPE) bearing high organized mesoporosity while addressing the SBA15-Si(HIPE) series.

## Graphical abstract

Taking inspiration from diatom hierarchically organized porosity, synthetic porous self-standing silica foams have been obtained through rational designs where sol-gel chemistry, emulsions, Pickering-based emulsions and lyotropic mesophases are advantageously combined.



**Keywords** Sol-gel process • Emulsions • Pickering emulsions • Lyotropic mesophases • Porous matter • Integrative chemistry

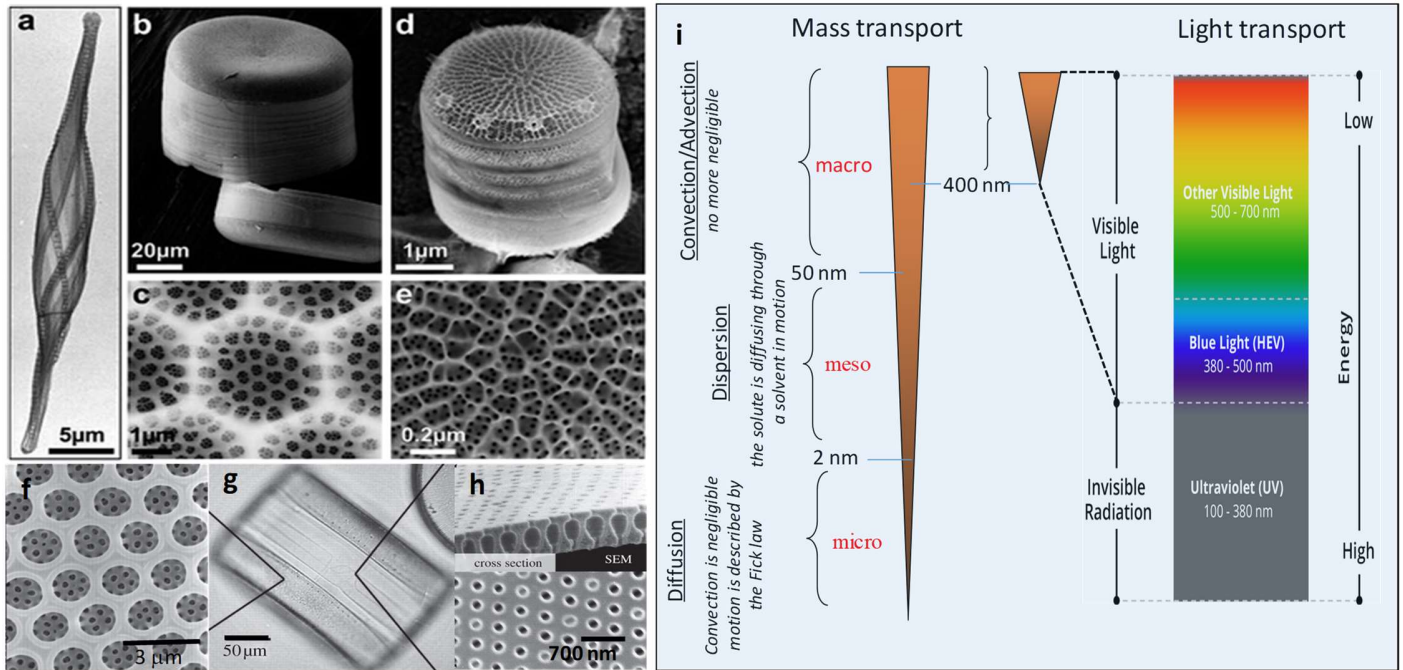
## Highlights

- Lyotropic mesophases, direct emulsions and sol-gel chemistry can be integrated toward the generation of self-standing foams where the macroscopic voids can be tuned while varying the starting emulsion volume fraction, addressing thereby the Si(HIPE) series.
- Pickering-based emulsions can be employed to shape macrocellular foams bearing high monodisperse character of both macroscopic cells and cell junction diameters, each feature being tunable independently, generating thus the Si(PHIPE) series.
- P123 nonionic surfactant,  $(\text{NH}_4)_2\text{SO}_4$  salt and direct emulsion are combined to generate self-standing monolith foams bearing a very high organization of the voids at the mesoscopic length, leading to the SBA15-Si(HIPE) series.
- Kosmotrope-Chaotrope balance is introduced in sol-gel chemistry as a tool to enhance silica polycondensation, beyond and additionally to the well-known salt screening and ionic strength effects.

## 1. Introduction

Today societal need is requesting the generation of smart materials being more and more complex, multi-scales, multifunctional, responsive toward external fields or even developing a certain degree of autonomy, taking inspiration from *Mother Nature*. Sol-gel chemistry is indeed the perfect chemical tool to generate such sophisticated materials. As occurring at low temperature this “Chimie Douce” [1-3] will not disrupt the organization of various templates occurring at various length scales. These templates might be supramolecular entities like micelles, but we can also include the whole field of the physical chemistry of complex fluids (air-liquid foams, biliquid foams, liquid crystals, hydrodynamic instabilities and so forth). To these shaping modes we can associate the application of external fields (electro-spinning, extrusion, spin-coating, spray-drying, 3D printing and so forth), in one word “technology”. Of course, in order to specify the final application, sol-gel chemistry is also ideal toward the generation of hybrid organic-inorganic materials or even living bio-materials. We can already sense that the chemical path to generate up-to-date advance functional materials is evidently complex, certainly interdisciplinary and possibly bio-inspired [4]. For instance, when considering the diatom frustule of the Figure 1a-h we can see that their silica exoskeletons are bearing a hierarchically organized porosity. If *Mother Nature* is constructing such sophisticated scaffolds, this is because at each level of porosity is occurring a specific functionality. This hierarchical porosity (Figure 1i) is at first glance important for many applications but is imperative when dealing with heterogeneous catalysis where exchange surface is involved. Considering the IUPAC nomenclature microporosity is addressing pores bearing diameters below 2 nm, mesoporous ones between 2 nm and 50 nm while all diameters above 50

nm are considered as macroporosity. Indeed, this IUPAC discrimination of pore sizes is directly related to the fluid hydrodynamics occurring at each level of porosity [5].



**Figure 1. 1** Structures of diatom cell walls. Electron microscopy images of isolated cell walls from different diatom species: a) *Cylindrotheca fusiformis*; b, c) *Coscinodiscus asteromphalus*; d, e) *Thalassiosira pseudonana*. RSC, Copyright 2004, f), Cell wall morphology of *Coscinodiscus wailesii* with valve and girdle patterns h), image taken by optical microscopy g) and details by scanning electron microscopy (f, h), i) scheme representing both the specific mass and light transport occurring at various length scales.

At the microscopic length scale, the fluid motion is driven only by diffusion and convection is negligible (molecular reactivity will occur at this length scale). At the macroscopic length scale, the fluid hydrodynamics is based only on convection with a basically Poiseuille flow (when fluids are Newtonian, this is to say that their viscosity remains constant under shear) and diffusion is now negligible considering the whole mass transport. At the mesoscopic length scale, the hydrodynamics is hybrid where the overall scenario can be regarded as a fluid moving through convection in which molecules are diffusing, this behavior is known as a dispersion flow. This is the reason why the hierarchical porosity from macroporous (optimizing the mass transport)

through microporous (where molecular reactivity occurs) is at first glance of importance for catalysis or energy conversion applications. Coming back to the diatom exoskeleton of Figure 1a-h we can notice a nano-porosity, this nano-porosity being somewhat organized and not totally randomly dispersed. Again if *Mother Nature* is doing so, this is not for the contemplative issue, but because the organization of the porosity at the nanoscale favors selective photonic behavior, where low energetic wavelengths (above 500 nm) will penetrate the skeleton while higher energetic wavelengths will not, protecting thus the diatom bioorganic counterpart (Fig 1i) for non-desirable energetic UV-light. Overall we can see that *Mother Nature* has optimized complex architectures where both, molecular reactivity and both mass and light transport are optimized as far as it can be. It is thus important, and challenging, to try to replicate such complex architectures in the Lab, way of thinking being bio-inspired, leading to the notion of chemistry of shapes.

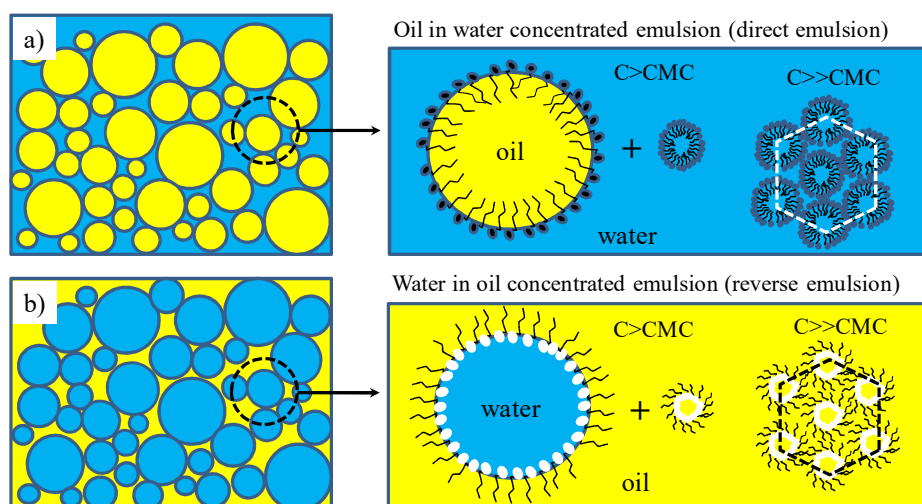
Inhere we focus on the coupling of sol-gel chemistry, direct concentrated emulsion employed as macroscopic molds and lyotropic mesophases as the mesoscale ones. We show how it is possible to conceive 3D-macrocellular monolithic foams bearing hierarchical porosities, through a fine coupling between the sol-gel process and the physical chemistry of complex fluids. In this mini-review we do not treat final applications on purpose, we stay at the chemistry of shapes level, while disregarding the *Integrative Chemistry* [6-7] concept dedicated toward a systemic approach of generating advanced functional materials.

## **2. Solid silica foams obtained by combining sol-gel process and emulsion templating**

### **2.1. Solid Foams, emulsion and lyotropic mesophase templates at a glance**

Foams are materials containing gaseous voids surrounded by a denser matrix, usually a liquid or a solid. Due to this specific structure they are widely used in applications like insulation (thermal and acoustic), absorbents and weight-bearing structures [8]. They are also employed to take benefit of their high specific surface in applications like heterogeneous catalysis and water cleaning [9]. Depending on their cell sizes, foams can be classified as macrocellular ( $>100\text{ }\mu\text{m}$ ), microcellular ( $1\text{-}100\text{ }\mu\text{m}$ ), ultramicrocellular ( $0.1\text{-}1\text{ }\mu\text{m}$ ) and nanocellular ( $0.1\text{-}100\text{ nm}$ ). Those cells can be close or open: in closed cells foams, the voids are isolated from each other and cavities are surrounded by complete cell walls whereas in open cell foams the structure consists mainly of ribs and struts. Polymers foams are the most common but their applications are limited by their inferior mechanical strength, poor surface quality and low thermal and dimensional stability. They are usually prepared by chemical or physical foaming [10], but the control of the cell size and morphology is difficult as well as the preparation of fully open-cell structures. Therefore, the emulsion-template approach to prepare foams may appear as an outstanding path for both mineral [11] or organic foams [12, 13] due to the possibility of better controlling the emulsions properties.

In this vein, High Internal Phase Emulsions (HIPE) are a class of emulsions characterized by an internal phase volume fraction exceeding 0.74, which corresponds to the most compact arrangement of uniform, undistorted spherical droplets (for a random packing the compact fraction is equal to 0.64). At higher volume fractions, their structure consists of deformed (polyhedral) and/or polydispersed droplets separated by a thin film of continuous phase, a structure resembling gas-liquid foams. Emulsions are classified into two categories depending on the nature of both the dispersed and continuous phases: water-in-oil (W/O) also called reverse emulsions and oil-in-water (O/W) also called direct emulsions (Scheme 1).



**Scheme 1.** Schematic representation of: a) Oil-in-water concentrated emulsion where oil droplets are dispersed within a continuous aqueous phase, b) water-in-oil concentrated emulsion where water droplets are dispersed within a continuous oily phase. The hydrophilic or hydrophobic continuous phase will contain respectively direct or reverse micelles (as soon as the surfactant concentration becomes larger than the critical micellar concentration (CMC)), a micelle being a supramolecular self-assembly of surfactant entities. For very high surfactant concentrations, these micelles can self-organize into lyotropic mesophases like a hexagonal phase in the present example. RSC Copyright 2011.

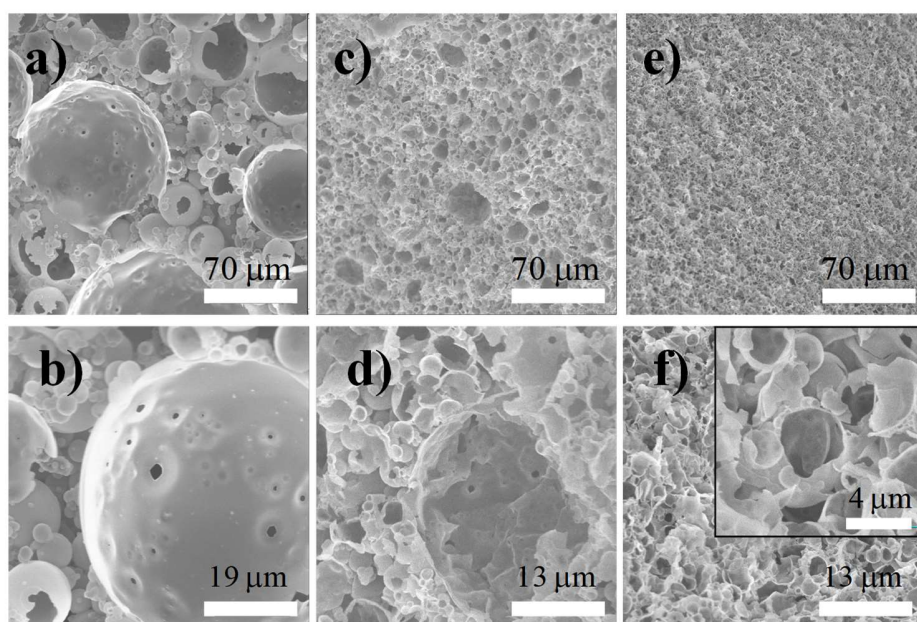
Emulsions are thermodynamically meta-stable systems, meaning that over time the emulsion will evolve until the dispersed and continuous phases macroscopically separate. To enhance their kinetic stability, surfactants are used to stabilize the oil/water interfaces. As shown in Scheme 1 those surfactant molecules constituted of a polar head group and a hydrophobic chain will adsorb at the oil/water interface to minimize the interfacial energy. The choice of the surfactant is important and the Bancroft rule states that the phase in which the surfactant is preferentially soluble becomes the continuous phase [14]. Also, micelles will be swollen with a small amount of the disperse phase, creating a microemulsion (nanometer length scale) which is thermodynamically stable contrary to a macro-emulsion (micrometer length scale). Considering their use as soft templates, these microemulsions will promote a second porosity, called mesoporosity, within the final materials after calcination. If the inorganic skeleton is amorphous as it the case for silica or polymer, final foams will bear intrinsic microporosity, leading overall to a hierarchical porosity.



## 2.2. Solid Foams, emulsion and lyotropic mesophase templates: The Si(HIPE) series

Materials synthesized from concentrated emulsions were labeled poly-HIPE (polymerized High Internal Phase Emulsion) and discovered by the industry [15] and very nice recent review articles have been proposed recently on this domain [16,17]. Such materials are most often obtained from the polymerization of a reverse concentrated emulsion, the continuous phase being composed of the organic polymerizable species [16,17]. Contrary to what is often admitted, the first inorganic-HIPE has also been pioneered by the industry [18]. Eight years later Imhof and Pine [19] published a paper exhibiting the advantage of working with monodisperse non aqueous emulsions. Our group has shown how the macroscopic voids can be tuned on demand either playing with the starting emulsion oil volume fraction, in order to make a parallel with the organic foams, we labeled those materials Si(HIPE) [20]. The first step is the hydrolysis of TEOS toward  $\text{Si}(\text{OH})_4$ , the silicic acid being the inorganic polymer precursor. Thereby, as the precursors are hydrophilic, oil droplet are dispersed within the continuous aqueous one, so that we are now dealing with direct emulsions (dispersion of oil droplets in water), see scheme 1. The Si-(HIPE) foams possess very high porosity and very low bulk density. The void size is usually situated in the microcellular range (1-100  $\mu\text{m}$ ). These materials will be used as supports for a wide range of applications. In order to tailor the macroporous solids for different applications, it is important to be able to modify the macroscopic void space diameters (Fig. 2). Varying the starting oil volume fraction ( $\phi_o$ ) of an oil-in-water concentrated emulsion [16] is one way to achieve that. Several O/W emulsions with increasing oil volume fractions (1Si-HIPE,  $\phi_o = 0.70$ ; 2Si-HIPE,  $\phi_o = 0.73$ ; and 3Si-HIPE,  $\phi_o = 0.78$ ) have been prepared and the resulting solid foams analyzed. Whatever the oil volume fraction, the general texture resembles aggregated hollow spheres. The macrocellular void

sizes of the resulting material diminish drastically because the viscosity of concentrated oil-in-water emulsions increases dramatically when the oil volume fraction reaches values above 0.64 [20]. The enhanced viscosity of the emulsions increases the shear applied to the droplets, thus inducing smaller macrocellular voids within the silica replica. These porous materials possess a secondary micro-mesoporosity, due to the lyotropic mesophase as explained previously. This secondary porosity results in specific surface areas (BET) values around  $800 \text{ m}^2 \text{ g}^{-1}$  addressing only  $100 \text{ m}^2 \text{ g}^{-1}$  of mesoporosity (BJH). It is possible to align the macropores by using a hydrophobic ferrofluid instead of oil and applying an external magnetic field during the condensation process [19].



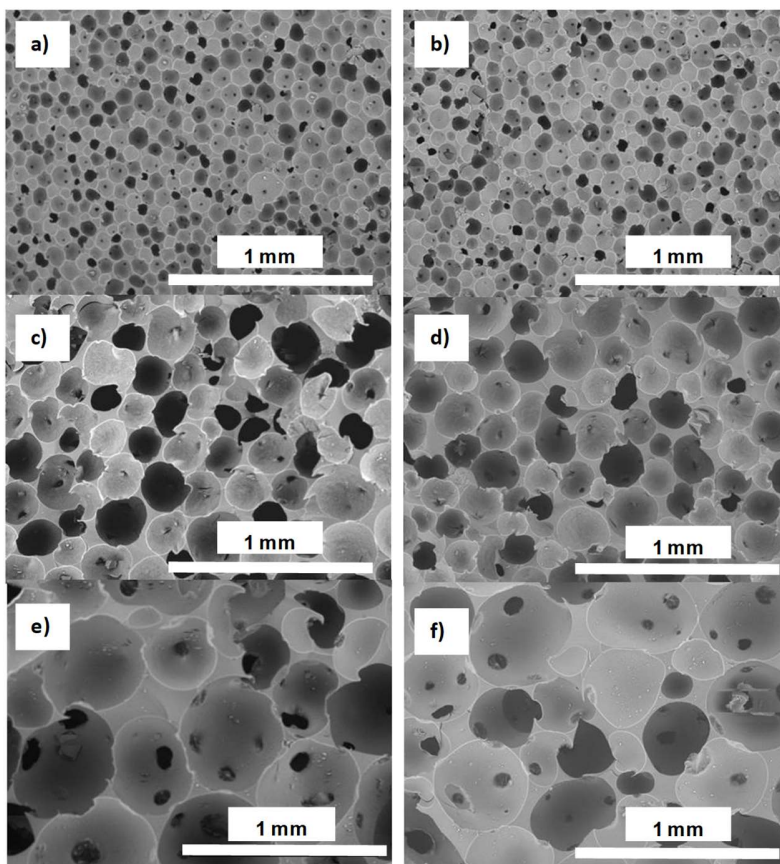
**Figure 2.** SEM visualization of the inorganic monolith-type material macrostructure. a) and b) 1Si-HIPE, c) and d) 2Si-HIPE, e) and f) 3Si-HIPE. RSC Copyright 2004.

As observed within Figure 2, the macroscopic cell diameters are rather polydisperse in size, we can express a strong monodispersity of the macroscopic cells while switching from surfactant-stabilized emulsion toward particles-stabilized ones. These Si(HIPE) materials can be easily

hybridized with organically modified silanes (OROMOSILs) to generated hybrid Organo-Si(HIPE) series fostering applications toward, photonic [22], heterogeneous catalysis whatever metallic [23], enzymatic [24] or bacteriologic [25]. These Si(HIPE) materials exhibited a low mesoporosity (around  $100 \text{ m}^2 \text{ g}^{-1}$  BJH surface area). Overall on a *Chemistry of Shapes* point of view two main challenges remained. The first one was to increase the monodisperse character of the macroscopic voids, and the second one was to enhance the Si(HIPE) mesoscopic surface area.

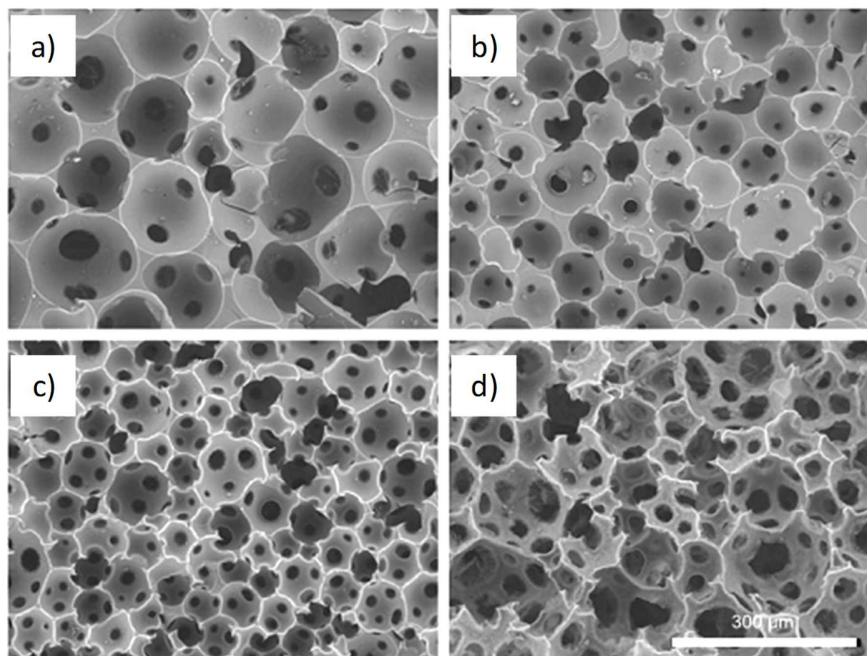
### **2.3. Solid Foams, Pickering emulsion templates: The Si(PHIPE) series**

Under this new configuration we are dealing with Pickering-based emulsions, that is to say emulsions stabilized by particles [26,27]. Thanks to the limited coalescence process occurring in Pickering emulsions, the oil droplets size may be easily tuned by the amount of particles [28]. This brings the advantage of an independent control over the initial oil volume fraction and the drop size. The sol-gel process is equivalent to the one described earlier and the resulting materials are noted PHIPE for Pickering-based HIPEs. For example, keeping the oil volume fraction fixed but varying the amount of nanoparticles in use, the drop size was varied and so did the resulting voids, ranging from 20 to 800  $\mu\text{m}$ , a macrocellular void size domain never reached before (Figure 3) with the Si-PHIPE series [29].



**Figure 3.** SEM images of solid foams synthesized from 64% PDMS-in-water emulsions: a) and b)  $7.3\text{Si(PHIPE)}_{64}$ , c) and d)  $3.7\text{Si(PHIPE)}_{64}$ , e) and f)  $2.5\text{Si(PHIPE)}_{64}$ . Materials are observed either after drying (a, c and e) or after thermal treatment (b, d and f). The emulsions are labeled  $X(\text{PHIPE})_Y$  where  $X$  is the amount of particles used to stabilize the emulsion with respect to the total oil weight ( $\text{mg g}^{-1}$ ),  $Y$  is the oil volume fraction (%) with respect to total sample volume Wiley Copyright 2012.

In addition to the void size, the size of the junction windows that connect adjacent macroscopic voids is of utmost importance as it governs the convectonal mass transport within the solid-state foams. The junction size can be triggered at constant initial drop size, that is to say at constant nanoparticle-to-oil weight ratio, by tuning the dispersed phase volume fraction (Fig. 4). Additionally, both parameters, void diameters and connecting windows can be tuned independently, offering thus a strong versatility toward the foams morphology. These Si PHIPE based foams can be further employed as hard templates for the design of carbonaceous foams, for biofuel cell application, with the advantage of tuning on demand the macroscopic mass transport.



**Figure 4.** SEM images of sintered solid foams synthesized from hexadecane-in-water emulsions containing an increasing internal phase volume fraction: a)  $_{2.6}\text{Si}(\text{PHIPE})_{64}$ , b)  $_{2.6}\text{Si}(\text{PHIPE})_{75}$ , c)  $_{2.6}\text{Si}(\text{PHIPE})_{85}$  and d)  $_{2.3}\text{Si}(\text{PHIPE})_{90}$ . The nomenclature is the same as the one adopted for Fig. 3. Copyright Wiley-VCH 2012.

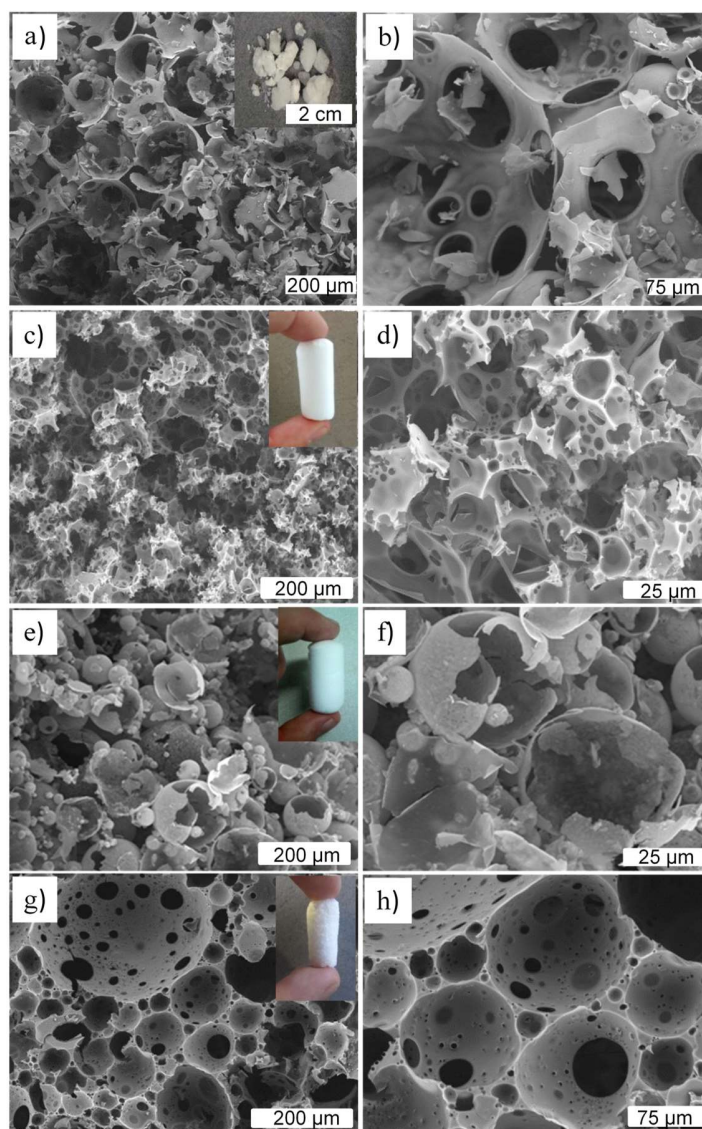
#### **2.4. Solid Foams, concentrated direct emulsions and P123 lyotropic mesophase templates: The SBA15-(PHIPE) series**

Ordered mesoporous silicates [30,31] have generated fascination in materials science and heterogeneous catalysis, as witness by thousands of publications in this domain. The interested reader can for example refer to [32-35]. These mesoporous materials were stated as outstanding candidates for extending heterogeneous catalysis or adsorbents for use in domains where pore sizes larger than those of zeolites were expected. Among the synthesized materials the most renowned are certainly the MCM-41 (Mobil Crystalline Materials) [36] using cetyltrimethylammonium as templating agent, SBA-15 (Santa Barbara Amorphous) [37] using triblock copolymer Pluronic 123

as meso-scale template, MSU (Michigan State University) [38] obtained from non-ionic polyoxyethylene alkyl ethers and HMS (Hexagonal Molecular Sieves) [39,40] where dodecylamine is employed as a mesoscale templating agent. The drawback is that obtaining self-standing monoliths and not only powders bearing hierarchical porosity is everything but an easy task to reach, in that vein we have to underline the Nakanishi and co-workers' highly efficient path to address monolith generation obtained by coupling sol-gel process, swelling lyotropic mesophases and phase separation instead of concentrated direct emulsions [41].

We have recently extended the SBA-15 mesoporous materials synthesis toward the generation of macro-mesocellular Si(HIPE) that we have labelled SBA15<sub>x</sub>-Si(HIPE) (Figure 5) where x represents the molar salt concentration. In our case we have employed a salt effect to promote efficient silica polycondensation while using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. We have demonstrated that this salt effect is not based only on the salt ionic strength but also on his chaotrope-kosmotrope character. Apart from electrostatic screening, ions are known for their ability to provoke order (kosmotrope) or disorder (chaotrope) following their position in the Hofmeister series [42]. For the anions the series follows : CO<sub>3</sub><sup>2-</sup> > SO<sub>4</sub><sup>2-</sup> > S<sub>2</sub>O<sub>3</sub><sup>2-</sup> > H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> ≈ NO<sub>3</sub><sup>-</sup> > I<sup>-</sup> > SCN<sup>-</sup> and for the cations : (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > K<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup> > Mg<sup>2+</sup> > Ca<sup>2+</sup> [37]. As seen on Figure 5 the salt concentration has a strong effect over both the macroscopic voids diameters and monolith self-standing properties.

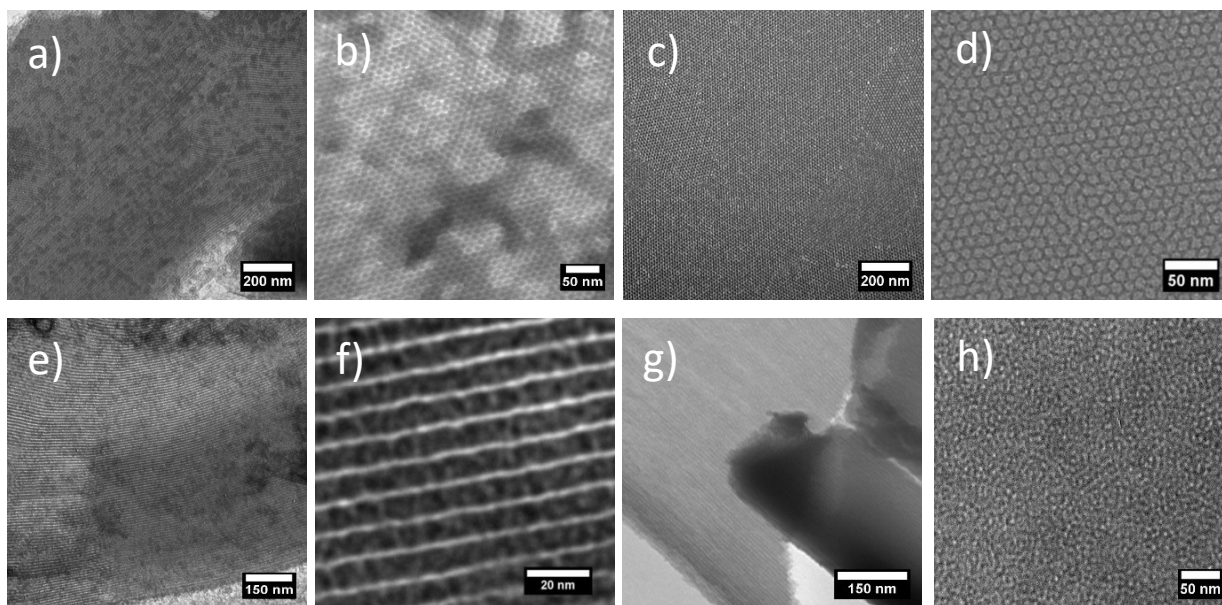




**Figure 5.** Overall appearance of the as-synthesized materials when varying the  $(\text{NH}_4)_2\text{SO}_4$  salt concentration. SEM visualization at different magnifications a-b) SBA-15<sub>0.1</sub>Si(HIPE), c-d) SBA-15<sub>0.5</sub>Si(HIPE), e-f) SBA-15<sub>1.0</sub>Si(HIPE), g-h) SBA-15<sub>2.0</sub>Si(HIPE). Inserts are photos of the materials showing whether they are self-standing or not. Copyright ACS 2018.

First, at the macroscale level, ammonium sulfate decreases the kinetic stability of the oil-in-water emulsion by changing the solubility of the P123 surfactant that precipitates inducing a decrease the surfactant density at the oil/water interface and the enhancement of coalescence. This phenomenon involves an increase on the cell diameter with the salt concentration. Second, at the

mesoscale level sulfate anions strengthen the hydrophobic interactions (salting out effect of sulfate anions) leading to a mesopore ordering as depicted in Figure 6.



**Figure 6.** TEM observations. a, b) SBA-15<sub>0.1</sub>Si(HIPE), c, d) SBA-15<sub>0.5</sub>-Si(HIPE), e, f) SBA-15<sub>1.0</sub>Si(HIPE) and g, h) SBA-15<sub>2.0</sub>Si(HIPE). ACS Copyright 2018.

The pore sizes distributions have been calculated through the B.J.H desorption curves. These pore sizes distributions reveal rather well-defined profile of the mesoscopic voids centered at the values ranging between 5 nm-9 nm. The BJH surface areas provide the mesoscopic surface with values ranging from 250 to 350 m<sup>2</sup> g<sup>-1</sup>, far above the ones obtained with the traditional Si(HIPE) series while employing TTAB (tetradecyltrimethylammonium bromide) as a mesoscopic templating agent [21]. Beyond the fact that we obtained self-standing macrocellular foams bearing organized 2D-hexagonal mesoporosity, it was the first time that the “kosmotrope-chaotrope” balance was introduced into the sol-gel process, beyond the well-known screening and ionic strength salt effects [43].



### 3. Conclusions

With this mini review we have emphasized the possibility to couple with a certain success sol-gel chemistry and the physical chemistry of complex fluid to chisel condensed matter at various length scales. Using various examples as traditional direct emulsions, Pickering emulsions and surfactant self-assemblies, we have shown that it is possible to combine all these systems to obtain materials perfectly controlled at all scales. Moreover these materials are modular according to the targeted applications. First, only classical direct emulsions were used for the synthesis of the Si(HIPE) series employing to tune the macroscopic void diameters and cationic surfactant molecules to both stabilize the emulsion oil/water interface at the macroscopic length scale and create vermicular poorly organized porosity at the mesoscopic length scale. The use of Pickering emulsions allowed us to reach macroporous size that have never been achieved before thanks to very large controllable droplets playing with the limited coalescence process. Controlling the initial drop size and dispersed phase volume fraction of surfactant-stabilized or particle-stabilized emulsion leads to independently tuning macroscopic cell diameters and cell junctions. Finally taking the synergetic effect of nonionic surfactants and a  $(\text{NH}_4)_2\text{SO}_4$  kosmotrope salt effect, we have shown that it is possible to obtained self-standing Si(HIPE) bearing high organized mesoporosity while addressing the SBA15-Si(HIPE) series. When considering the diatom exoskeleton of the Figure 1 and comparing the morphologies with the Si(HIPE), Si(PHIPE) and SBA15-Si(HIPE) series, we understand very easily that the next step is to combine very high monodisperse void and cell junction diameters at the macroscopic length scales with a very high organization of the mesoscopic porosity. In brief the SBA15-Si(PHIPE) series is still missing where all the porosity will be organized on demand at various length scales, proposing potentially the first synthetic silica-diatom-exoskeleton. Up to now, when operating this complex synthetic

approaches, we were completely driven by the thermodynamic equilibrium in term of silica synthesis (emulsion preparation being governed by kinetics). Maybe, sooner or later it would be interesting to perform sol-gel route out of this thermodynamic dead end while promoting continuous chemical reactions driven by kinetics rather than thermodynamics, feature that *Mother Nature* is mastering since a certain time scale.

### Acknowledgments

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### References

1. Livage J (1977), Vers une chimie écologique. Quand l'air et l'eau remplacent le pétrole, Le Monde.
2. Brinker CJ, Scherrer GW (1990), The Physics and Chemistry of Sol-Gel Processing, Academic, San Diego
3. Livage J, Henry M, Sanchez C (1988) Sol-gel chemistry of transition metal oxides. Prog. Solid State Chem. 18:259–342
4. Mann S, Ozin GA (1996) Synthesis of inorganic materials with complex form. Nature. 382:313–318
5. Guyon, E, Hulin JP, Petit L, Mitescu CD (2001) In Physical Hydrodynamics; *Oxford University Press*
6. Backov R (2006) Combining soft matter and soft chemistry: integrative chemistry towards designing novel and complex multiscale architectures. Soft Matter. 2:452-464
7. Faustini M, Grosso D, Boissière C, Backov R, Sanchez C (2014) “Integrative Sol–gel Chemistry”: A Nanofoundry for Materials Science. J. Sol-Gel Sci. Technol. 70:216-226
8. Klemper D, Frisch K.C (1991), Handbook of polymeric foams and foam technology; Oxford University Press

9. Rosa M.E (2008), *Phil. Mag. Lett.* 88:637-645
10. S.-T. Lee, N. S. Ramesh (2009), *Polymeric Foams: Mechanisms and Materials* **2<sup>nd</sup> Ed**; *CRC Press Boca Raton Fl*
11. Esquera J, Solans C (2006), *Surf. Sci. Series.* 132:245-261
12. Ceglia G, Mahéo L, Viot P, Bernard D, Chirazi A, Ly I, Mondain-Monval O, Schmitt V (2012) Formulation and mechanical properties of emulsion-based model polymer foams. *Eur. Phys. J. E* 35
13. Quell A, Elsing J, Drenckhan W, Stubenrauch D (2015) Monodisperse Polystyrene Foams via Microfluidics – A Novel Templating Route. *Adv. Eng. Mater.* 17:604-609
14. Bancroft W.D (1913) The Theory of Emulsification, V. *J. Phys. Chem.* 17:501-519
15. Barby D, Haq Z (1982) *Eur. Patent Appl.* 60138
16. Silverstein MS (2014) PolyHIPEs: recent advances in emulsion-templated porous polymers. *Prog. Polym. Sci.* 39:199–234
17. Silverstein MS (2017) Emulsion-templated polymers: Contemporary contemplations. *Polymer*, 126:261–282
18. Araya A (1989) Hydrophobic, highly porous, three-dimensional inorganic structures. *US Patent*, 4888309
19. Imhof A, Pine D (1997) Ordered macroporous materials by emulsion templating. *Nature*, 389:948-951
20. Carn F, Colin A, Achard MF, Deleuze H, Sellier E, Birot M, Backov R (2004) Inorganic monoliths hierarchically textured via concentrated direct emulsion and micellar templates. *J. Mat. Chem.* 14:1370-1376
21. Carn F, Colin A, Schmitt V, Leal-Calderon F, Backov R (2005) Soft matter, sol–gel process and external magnetic field to design macrocellular silica scaffolds. *Colloid. Surface. A.* 263:341-346
22. Brun N, Julian-Lopez B, Hesemann P, Guillaume L, Achard MF, Deleuze H, Sanchez C, Backov R (2008) Eu<sup>3+</sup>@Organo-Si(HIPE) Macro-Mesocellular Hybrid Foams Generation: Syntheses, Characterizations, and Photonic Properties. *Chem. Mater.* 20:7117-7129
23. Ungureanu S, Birot M, Deleuze H, Babot O, Achard MF, Popa MI, Sanchez C, Backov R (2010) Palladium nanoparticles heterogeneous nucleation within organically grafted silica

- foams and their use as catalyst supports toward the Suzuki–Miyaura and Mizoroki–Heck coupling reactions. *Appl. Catal. A*. 390:51-58
24. Brun N, Babeau-Garcia A, Achard MF, Sanchez C, Durand F, Laurent G, Birot M, Deleuze H, Backov R (2011) Enzyme-based biohybrid foams designed for continuous flow heterogeneous catalysis and biodiesel production. *Energy Environ. Sci.* 2011, 4:2840-2844.
  25. Roucher A, Morvan M, Pekin D, Depardieu M, Blin JL, Schmitt V, Baret JC, Backov R (2018) From Compartmentalization of Bacteria within Inorganic Macrocellular Beads to the Assembly of Microbial Consortia. *Adv. Biosys.* 2
  26. Ramsden, W. (1903) Separation of Solids in the Surface-Layers of Solutions and 'Suspensions' (Observations on Surface-Membranes, Bubbles, Emulsions, and Mechanical Coagulation).- Preliminary Account. *Proc. R. Soc. Lond.* 72: 156–164.
  27. Pickering SU (1907) CXCVI.—Emulsions. *J. Chem. Soc., Trans.* 91:2001-2021
  28. Arditty S, Whitby C.P, Binks B.P, Schmitt V, Leal-Calderon F (2003) Some general features of limited coalescence in solid-stabilized emulsions. *Eur. Phys. J. E.* 11:273-281
  29. Destribats M, Faure B, Birot M, Babot O, Schmitt V, Backov R (2012) Tailored Silica Macrocellular Foams: Combining Limited Coalescence-Based Pickering Emulsion and Sol–Gel Process. *Adv. Funct. Mater.* 22:2642-2654
  30. Beck J.S, Vartuli J.C, Roth W.J, Leonowicz M.E, Kresge C.T, Schmitt K.D, Chu C.T.-W, Olson D.H, Sheppard E.W, McCullen S.B, Higgins J.B, Schlenker J.L (1992) A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.* 114:10834-10843
  31. Di Renzo F, Cambon H, Dutartre R (1997) A 28-year-old synthesis of micelle-templated mesoporous silica. *Microporous Mater.* 10:283-286
  32. Taguchi A, Schüth F (2005) Ordered mesoporous materials in catalysis. *Microporous Mesoporous Mater.* 77:1-45.
  33. E. Davis M (2002) Ordered porous materials for emerging applications. *Nature.* 417:813-821
  34. Balas F, Manzano M, Horcajada P, Vallet-Regi M (2006) Confinement and Controlled Release of Bisphosphonates on Ordered Mesoporous Silica-Based Materials. *J. Am. Chem. Soc.* 128:8116-8117

35. G. Trewin B, I. Slowing I, Giri S, Chen HT, Lin V (2007) Synthesis and Functionalization of a Mesoporous Silica Nanoparticle Based on the Sol–Gel Process and Applications in Controlled Release. *Acc. Chem. Res.* 40:846–853
36. Kresge C.T, Leonowicz M.E, Roth W.J, Vartuli J.C, Beck J.S (1992) Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature.* 359:710-712
37. Zhao D, Feng J, Huo Q, Melosh N, Fredrickson G.H, Chmelka B.F, Stucky G.D (1998) Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. *Science.* 279:548-552
38. Bagshaw S.A, Prouzet E, Pinnavaia T.J (1995) Templating of mesoporous molecular sieves by nonionic polyethylene oxide surfactants. *Science.* 269:1242-1244
39. Tanev P.T, Pinnavaia T.J (1995) A Neutral Templating Route to Mesoporous Molecular Sieves. *Science.* 267:865-867
40. Boissière C, Martines M.A.U, Tokumoto M, Larbot A, Prouzet E (2003) Mechanisms of Pore Size Control in MSU-X Mesoporous Silica. *Chem. Mater.* 15:509–515
41. Amatani T, Nakanishi K, Hirao K, Kodaira T (2005) Monolithic Periodic Mesoporous Silica with Well-Defined Macropores. *Chem. Mater.* 17:2114-2119
42. Hofmeister F (1888) Zur Lehre von der Wirkung der Salze. *Arch. Exp. Pathol. Pharmacol.* 24:247-260
43. Roucher A, Bentaleb A, Laurichesse E, Dourges M.A, Emo M, Schmitt V, Blin JL, Backov R (2018) First Macro-Mesocellular Silica SBA-15-Si(HIPE) Monoliths: Conditions for Obtaining Self-Standing Materials. *Chem. Mater.* 30:864-873