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# Micrometric Monodisperse Solid Foams as Complete Photonic Bandgap Materials

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**KEYWORDS** 3D solid foams, self-assembly, microfluidics, polymers, photonic band gaps

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**ABSTRACT:** Solid foams with micrometric pores are used in different fields (filtering, 3D cell culture, etc.), but today, controlling their foam geometry at the pore level, their internal structure, and the monodispersity, along with their mechanical properties, is still a challenge. Existing attempts to create such foams suffer either from slow speed or size limitations (above 80  $\mu\text{m}$ ). In this work, by using a temperature-regulated microfluidic process, 3D solid foams with highly monodisperse open pores (PDI lower than 5%), with sizes ranging from 5 to 400  $\mu\text{m}$  and stiffnesses spanning 2 orders of magnitude, are created for the first time. These features open the way for exciting applications, in cell culture, filtering, optics, etc. Here, the focus is set on photonics. Numerically, these foams are shown to open a 3D complete photonic bandgap, with a critical index of 2.80, thus compatible with the use of rutile  $\text{TiO}_2$ . In the field of photonics, such structures represent the first physically realizable self-assembled FCC (face-centered cubic) structure that possesses this functionality.

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## INTRODUCTION

Solid polymer foams are widely used in a variety of fields such as insulation, packaging, electronic and biomedical applications.<sup>1,2</sup> Indeed, they combine the remarkable features of liquid foams in terms of lightness, high surface area, tunable porosity and topological organization with interesting stiffness properties. Depending on the application, the required structural properties vary, especially the pore size and the wall thickness, which makes the fabrication process critical. Different conventional and advanced processing techniques have been developed to obtain such structures with customized properties.<sup>3</sup> However, none of them succeeded in downscaling the foam pore size to few micrometers, while keeping control over the pore size and the stiffness, which dramatically limits their potential. All existing methods of 3D solid polymer foam fabrication generate strong inhomogeneity when targeting foams with pore sizes smaller than 80  $\mu\text{m}$ .<sup>4</sup> Although adequate for a range of applications, this polydispersity becomes detrimental when highly controlled structures are needed. Different domains such as photonics, 3D cell culture, or filtering would considerably benefit from the availability of solid foams with highly tunable monodisperse pores of few micrometers. For example, for 3D cell cultures embedded within a solid polymer foam, it would be advantageous to

cover a large range of micrometric pore sizes in a way that matches the diversity of cells dimensions.<sup>1, 3, 5</sup>

Recently, 2D foams with controlled pore size distribution<sup>6</sup> have been demonstrated to exhibit outstanding photonic properties, hence raising the possibility of employing 3D solid polymer foams as templates for Photonic Band Gap (PBG) materials.<sup>7-18</sup> Such materials prevent the propagation of electromagnetic waves in a frequency range called a band gap. The fabrication of polymer based photonic materials<sup>10, 19-26</sup> in the near infrared and the visible range has been developed.<sup>27</sup> Among the explored configurations, rod-connected lattices<sup>28, 29</sup> showed the best photonic performances. They exhibited a full PBG at lower refractive index,<sup>30</sup> enlarging the width of PBG for refractive index of 3.6<sup>31</sup> and getting higher mid-gap center frequency. Such rod-connected lattices are a feature of 3D open cell foams where plateau borders self-assemble into well-organized structures.<sup>32</sup> However, even though the photonic diamond network was introduced almost 30 years ago<sup>28</sup> and despite decades of active research in the field,<sup>33-36</sup> the physical realization of self-assembled photonic structure with a complete photonic band gap remains elusive.

In this article, we explore physically realizable 3D polymer solid foams as a new potential class of PBG materials that can be accurately self-assembled and downscaled by using

microfluidics, without increasing the complexity of the unit cell structure. To produce 3D solid foams with tunable properties, microfluidics, combined with liquid templating routes, has already tentatively been used.<sup>37-40</sup> In References<sup>4, 37-40</sup>, monodisperse solid foams were obtained by using a Flow Focusing (FF) microfluidic device, and cross-linking the polymer aqueous solutions to solidify the material. However, solidification-induced clogging issues prevented from obtaining monodisperse solid foams with pores smaller than 80  $\mu\text{m}$ .<sup>4</sup> In the present work, we solve this problem by developing a temperature-regulated microfluidic process to tune the solidification along the fabrication process. Consequently, monodisperse solid foams with a Polydispersity index (PDI) less than 10 %, covering a pore size range from 5  $\mu\text{m}$  to 400  $\mu\text{m}$ , and with stiffnesses spanning 2 orders of magnitude were obtained.

Here, we uncover an outstanding photonic potential of these foams. We numerically show that 3D solid FCC (Face-centered cubic, Kepler structure) foams, explored for the first time here, exhibit 3D complete photonic band gaps in a range of refractive index compatible with existing materials, a property that previous self-assembled structures were unable to match. Our work thus opens a new route for fabricating self-assembled complete photonic band gap materials.

## RESULTS AND DISCUSSION

Figure 1a shows the Flow Focusing microfluidic device used to produce the solid polymer foams discussed here (see Supporting Information, SI1). First, a liquid polymer foam is generated at low temperature (10°C), using gas volume fractions above the jamming point.<sup>41</sup> In such conditions, bubbles self-assemble in monodisperse and ordered patterns (inset, Figure 1a). The resulting liquid polymer foam is spread over a glass plate and then exposed to a temperature of 70 °C. This step toughens the structure, thus avoiding the formation of heterogeneity induced by liquid foam aging. The process forms a few (2-3) bubbles layer foam. It can be repeated several times to obtain a thicker solid foam (see Supporting information, SI3). Following this procedure and using one microfluidic generator (one nozzle), a crosslinked foam sample of 2  $\text{cm}^3$  (with pore sizes = 100  $\mu\text{m}$ ) can be produced in 1 hour. The parallelization of 5-10 microfluidic chips would allow us to multiply the produced volume accordingly. The obtained monodisperse foams are locally ordered (Figure 1b) and, in agreement with the literature, organize into two stable crystalline structures depending on the filling fraction. At high filling fraction (wet state) the system self-organizes into a Face-Centered Cubic Structure (FCC, Kepler structure) while at low filling fraction (dry state), the foam is a Body-Centered Cubic structure (BCC, Kelvin structure).<sup>42</sup> As shown in Figure 1c and 1d, for a filling fraction  $\phi$  above 9% a FCC-like structure is observed (Figure 1c,  $\phi=11\%$ ), whereas for  $5\% < \phi < 9\%$  (Figure 1d,  $\phi=8\%$ ), a transition between the dry and the wet states occurs and a coexistence of BCC and FCC structures is obtained; finally, for  $\phi < 5\%$ , BCC-like structures are obtained.<sup>40, 43</sup>

The pore sizes of the 3D solid foams are varied by adjusting the channel dimensions (see Supporting Information,

SI1), flow pressures and reactant concentrations. Figure 2a-d show confocal transmission images of 3D solid foams with a pore size ranging from 400  $\mu\text{m}$  down to 5  $\mu\text{m}$ . All the designed foams pores size distributions follow a normal distribution with polydispersity indices (i.e. normalized size standard deviation) of few percent (2% in Figure 2e). Figure 2f-h, show SEM images of 3D chitosan solid foam with different layers of interconnected open pores ranging from 100 $\mu\text{m}$  to 5  $\mu\text{m}$ . The films separating the bubbles completely disappear during the foam preparation, so that the gas phase percolate withing the structure, making the structure suitable for the photonic application. Indeed, closed cell foams do not open any PBG (see Supporting Information, SI9). The mechanical behavior of foam samples (e.g. Figure 2i) at different cross-linker concentrations under compression is showed in Figure 2j. As commonly observed with foams, different regions can be individuated in the curves<sup>44</sup> (Figure 2j). In order to estimate the elastic modulus  $E$ , the elastic region at low strain is taken into consideration. Results show that the elastic modulus  $E$  spans a range of two orders of magnitude (respectively from about  $10^3$  to  $10^5$  Pa in Fig. 2j), by increasing the amount of cross-linker. Consequently, it is noteworthy that the described microfluidic process allows a tuning of the mechanical properties, which can be necessary for material handling and manipulation as in photonic devices. The access to a material with a large range of elasticities is crucial for other applications where the mechanical behavior is a main functionality like in 3D cell culture for tissue engineering.<sup>5</sup>

The structures in the confocal images of Figure 1 and 2 are composed of ordered layers in the out-of-plane direction of depths typically larger than 4-5 layers, a number above the evanescent penetration depth (3.2 layers, see Experimental Section). Consequently, we infer that the electromagnetic field vanishes out in the band gap within the first encountered layers. The obtained solid structure shares the topological and geometric features of the original liquid foam template: the Plateau Borders (PB) thicken in the close vicinity of the nodes but are of a constant diameter in most of the central region, i.e. on two-third of the PB length  $\pm 15\%$  (see Supporting Information, SI4).

To fully explore the potential of the fabricated foams for photonic applications, we simulate the electromagnetic response in foam configurations. Guided by the experiments, we restricted ourselves to the study of observed structures, i.e. Kelvin and Kepler foams. Indeed, another interesting structure called Weaire-Phelan foam and that is more energetically favorable,<sup>43,45</sup> exhibits a significantly wide complete photonic bandgap.<sup>33-36</sup> However, from an experimental prospective and contrarily to Kelvin and Kepler structures, this foam does not form spontaneously and needs a forcing to exist. This feature raises serious experimental challenges for its fabrication.<sup>46</sup> The Kelvin structure also presents a photonic bandgap but it has rather limited width.<sup>33</sup> The band structure of Kepler foam remains unknown. We model Kepler (FCC) and Kelvin (BCC) structures by networks of connected rods of diameter  $d$  and relative dielectric constant  $\epsilon$  embedded within a unit cell of size  $a$ . The remaining volume is occupied by air of relative

dielectric constant  $\epsilon_{\text{air}} = 1$  (see Supporting Information, SI6). We numerically investigate the optical properties of the two structures represented in Figure 3a and 3c. The band structure is found by numerically solving Maxwell's equations through finite-element eigenmode decomposition with periodic boundary conditions<sup>47</sup> and with the spectral MPB method,<sup>48</sup> two approaches that are found in excellent agreement (see Supporting Information, SI6). We investigate the band structure as a function of the dimensionless frequency  $f = \omega a / (2\pi c)$  with  $\omega$  the frequency and  $c$  the speed of light. The band diagram of the FCC structure in Figure 3b shows the presence of a complete band gap with a gap-midgap  $\%BG = \frac{\text{band width}}{\text{mean } f \text{ in the BG}} = 8.95$ . Similarly, we numerically compute the band structure of the BCC structure and observe, as shown in Figure 3d, a complete BG opening, with  $\%BG = 3.35$ . The crossing of bands in Figure 3b and 3d indicates a triple degeneracy at the points of the Brillouin zone which is expected as a natural consequence of the three four-fold rotational symmetry of the unit cell.<sup>49</sup> Notably, for both structures, the band gap does not close along the standard paths of the Brillouin zone (upper edges of the band gap occur along edges of the irreducible Brillouin zone), a result that has been confirmed by Density of States (DOS) calculations (see Supporting information, SI8). Furthermore, we find no significant influence of the rods and the vertices geometries on the bandgap width, we pursue our numerical investigation modeling foam Plateau borders as cylindrical rods (see Supporting Information, SI10). We numerically explore in Figure 4a the dependence of the gap-midgap ratio on the geometrical and optical parameters of the unit cell. Maxwell's equations are scale invariant so that the band gap depends only on the dimensionless rod's diameter  $\tilde{d} = d/a$  and on the optical index  $n = \sqrt{\epsilon}$  of the rods. For a given rod optical index, we vary the rod diameter and measure the corresponding  $\%BG$ . For both structures we observe that above a critical index a large band gap opens for a pronounced range of rod diameter. In both structures, an optimal rod diameter is found as a function of its optical index. We also note that for a given index, the  $\%BG$  is always larger for an FCC structure than for a BCC structure. Figure 4a shows an increase in  $\%BG$  with the optical index and more importantly a critical optical index ( $n^*$ ) below which the band gap closes. In Figure 4b we investigate the evolution of the maximum  $\%BG$  with the rods index for both the FCC and BCC structures. The  $\%BG$  increases with the optical index and a critical index threshold is evidenced  $n^* = 2.80$  for FCC and  $n^* = 3.21$  for BCC. It is noteworthy recalling that large optical index contrasts are usually required to open band gaps. For example, for the inverse opal structure,<sup>50</sup> a band gap opens for an optical index contrast larger than 2.92. In contrast, Figure 4b shows that FCC solid foam exhibits a critical index  $n^* = 2.80$  which makes it possible, for the first time, to open a band gap using the rutile  $\text{TiO}_2$  for example ( $n = 2.9$ ), a key result of this investigation. The mechanism of the band gap opening can be rationalized by exploring the spatial distribution of the field mode intensity of the dielectric and the air band,<sup>49</sup> the band respectively below and above the gap. For the air band, the field intensity is concentrated into region of small dielectric constant.

Conversely, for the dielectric band the field intensity is concentrated into region of large dielectric constant. This field concentration into different dielectric areas is driven by the dielectric contrast between these two areas. Therefore, for large dielectric contrast the coexistence of the dielectric and air bands is precluded in the frequency domain and a band gap opens (see Supporting Information, SI7).<sup>49</sup> Coincidentally and in striking contrast with the BCC phase, the FCC structure combines all possible advantages: it is obtained in a pure configuration (Figure 1c), it exhibits larger PBG (Figure 3b), which occurs at a lower critical optical index contrast (Figure 4b).

## Conclusion

To conclude, we have successfully fabricated unprecedented highly monodisperse 3D solid foams, in the micrometric range (pore size 5–400  $\mu\text{m}$ ). These foams can be used as templates for complete photonic band gaps structures. The temperature-regulated microfluidic approach used to fabricate these solid foams solves the fabrication issues that thus far prevented their miniaturization. These new physically realizable structures that display photonic band gaps for an index contrast of 2.80 represent a substantial progress in the field of self-assembled photonic band gap materials. These foams open up numerous applications in the infrared (IR) domain where they can be used as templates for cooling materials (blocking infrared radiations) in the building industry or as angle-independent LiDAR filters for autonomous vehicles in the mass automotive market. The IR domain is highly demanding for new innovations and remains more accessible than the “visible” market saturated by well-established silicon-based technologies.

Still, the obtained solid foams could be further downscaled by combining the process described here with the standard downscaling methods existing for liquid emulsions.<sup>51</sup> This task is achievable with lithography techniques and can be facilitated by using step-emulsification configuration, which produces submicron droplets with high throughput. Bubbles of 400 nm would lead to a band gap centered on 500 nm, as mentioned above. At this wavelength, the refractive index of rutile  $\text{TiO}_2$  is close to 2.9. Therefore, the foam template will have to be coated with high refractive index materials using dip-coating or physical vapor deposition techniques like sputtering. This has been tentatively explored and preliminary results are showed in Supporting Information, SI5. Otherwise, the polymer forming the 3D foam template will have to be substituted by rutile  $\text{TiO}_2$ , a process finely reported by Muller et al.<sup>52</sup> These numbers indicate that our foam technology has a serious potential to create a complete PBG material in the visible range.

Although we focused on its photonic band gap, the interest for the proposed micrometric foams is not restricted to this domain. The access to 3D solid polymer foams with a high tunability in terms of pore size and mechanical properties opens other applications such as 3D cell culture for tissue engineering and regenerative medicine.

## EXPERIMENTAL SECTION

**Foam fabrication process.** Monodisperse liquid foam generation is carried out in a Flow Focusing microfluidic geometry (Figure 1a). The device is made by standard soft photolithography and replica-molding techniques using polydimethylsiloxane (PDMS). The channels have a depth of 5-50  $\mu\text{m}$  and a width of 5-400  $\mu\text{m}$  depending on the desired pore size (see Supporting Information, SI1). The setup contains two inlets for injecting the liquid and the gas phases respectively through plastic tubes, and an outlet tube for foam collection. The gas phase is nitrogen with traces of perfluorohexane  $\text{C}_6\text{F}_{14}$  in order to hinder Ostwald ripening.<sup>38</sup> The liquid phase is an aqueous solution of chitosan ( $M_w = 0.3 \cdot 10^6$  g/mol, Sigma Aldrich), a biopolymer extracted from shrimp shells, at a concentration varying between 0.3 and 1 %w/v in milliQ water. Acetic acid is added to the solution at a concentration of 0.1 mol/L. Lutensol AT25 (provided by BASF), a non-ionic surfactant, is added at a concentration of 4 g/L. The surfactant permits stabilization of the liquid/air interface. Dissolution and homogenization are obtained by stirring for at least 2 days at room temperature. The crosslinking agent Glyoxal (40% in water, purchased from Sigma Aldrich) is added at low temperature to the liquid phase at a concentration varying between 2 and 50 %v/v. The obtained liquid phase is kept in an ice bath in order to prevent the crosslinking.

At the nozzle where the gas phase meets the liquid phase, micro-bubbles of gas are encapsulated in the continuous liquid phase. A bubble generation frequency between 400-800 bubbles per second is obtained depending on the gas and liquid pressures. The flows are pressure-driven at a pressure  $p_{\text{gas}}$  and  $p_{\text{liq}}$  (0.05 - 5 bar) using a MFCS™-EZ pressure controller system (Fluigent) connected to a nitrogen tap. The temperature of the microfluidic chip is fixed at 5-10 °C using a Peltier device in order to prevent crosslinking inside the microfluidic chip. The thus obtained liquid foam layer can then be heated at a temperature between 50 and 100 °C, thus above the chitosan crosslinking temperature (40 °C)<sup>53</sup> for 1-5 minutes. For the samples presented here, the temperature was set at 70 °C. For a thin sample (under 1-3 mm in height), the crosslinking takes 2-3 min. For larger samples, a layer-by-layer procedure is followed (see Supporting Information, SI2 and SI3). The in-situ foam generation is tracked using an Optical Microscope (Leica) with 4-20x scanning objectives.

**Morphological characterization.** To characterize the solid foam morphology, the sample is placed on a microscope glass slide and images are taken using Optical and Confocal microscope systems (Leica) taking advantage of the auto-fluorescence of chitosan (in green). For confirmation, the morphological characteristics of the solid foams were also checked using Scanning Electron Microscope (SEM, FEI Magellan400 at 5-10 kV). Images are analyzed by using a Matlab code that allows studying the topology of the foam (pore size distribution, PB profile in Supporting Information, SI4).

**Mechanical characterization.** In order to determine the elastic modulus of the fabricated foams, compression tests are performed on different solid chitosan foams samples

containing different concentrations of cross-linker (from 100 to 400  $\mu\text{L}$  of Glyoxal in 1 mL of chitosan solution at 0.6% wt). An Instron 5865 universal testing machine with a 500 N load cell is used. The compression rate is 10 mm/min. Each test is conducted three times. The elastic modulus  $E$  is calculated as the slope of the linear elastic region (at low strain, under 15%) in the stress-strain curves.

**Photonic band gap simulation.** Band structure and photonic eigenmode are calculated using spectral methods with a planewave basis (MPB software package).<sup>48</sup> We employ a 128x128x128 spatial mesh and a corresponding planewave basis consisting  $\sim 2 \times 10^6$  k-vectors, which ensures full convergence of the band structure calculation results. The band structure calculation results shown above are fully confirmed through finite element package Comsol Multiphysics (ver.5.4) (see Supporting Information, SI6).

**Estimation of the penetration depth of the FCC structure in the band gap.** At the bottom of the air band the penetration depth<sup>(23)</sup>  $\delta \approx \left(\frac{\alpha}{\Delta f}\right)^{-1/2}$  with  $\alpha = \frac{\partial^2 f}{\partial k^2}$  the local curvature along a given wave vector path and  $\Delta f \approx 5 \cdot 10^{-2}$  corresponding to half of the bandgap width. The bottom of the air band occurs along the wave vector path  $\Gamma$ -K and we estimate  $\delta \approx 3.2 \pm 0.1$  [unit cell].

## SUPPORTING INFORMATION

Supporting Information is available free of charge on the ACS Publications website at DOI: xxx

- Geometrical characteristics of the used microfluidic devices; Crosslinking methods and layer-by-layer solidification process for foam sample; Plateau Border thickness profile analysis; Coating of the 3D solid polymer structure; Band diagram using *Comsol Multiphysics*; Numerical field distribution analysis; Density of States Calculations; Band diagram for closed cell foam; Distorted Network Decorations.

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### Author Contributions

IM, MR carried out the experimental work; MM, GL performed the simulations; JC contributed in the synthesis of materials; KM contributed to the research; IM, MM, MR, GL, MF, ML, PT interpreted the results; MF, ML, PT supervised the research project; IM, MR, MF, ML, PT prepared the manuscript. IM, MM, MR contributed equally to this work.

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## DATA AVAILABILITY

The data underlying the findings of this study are available without restriction.<sup>54</sup>

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**Figures**  
Figure 1.

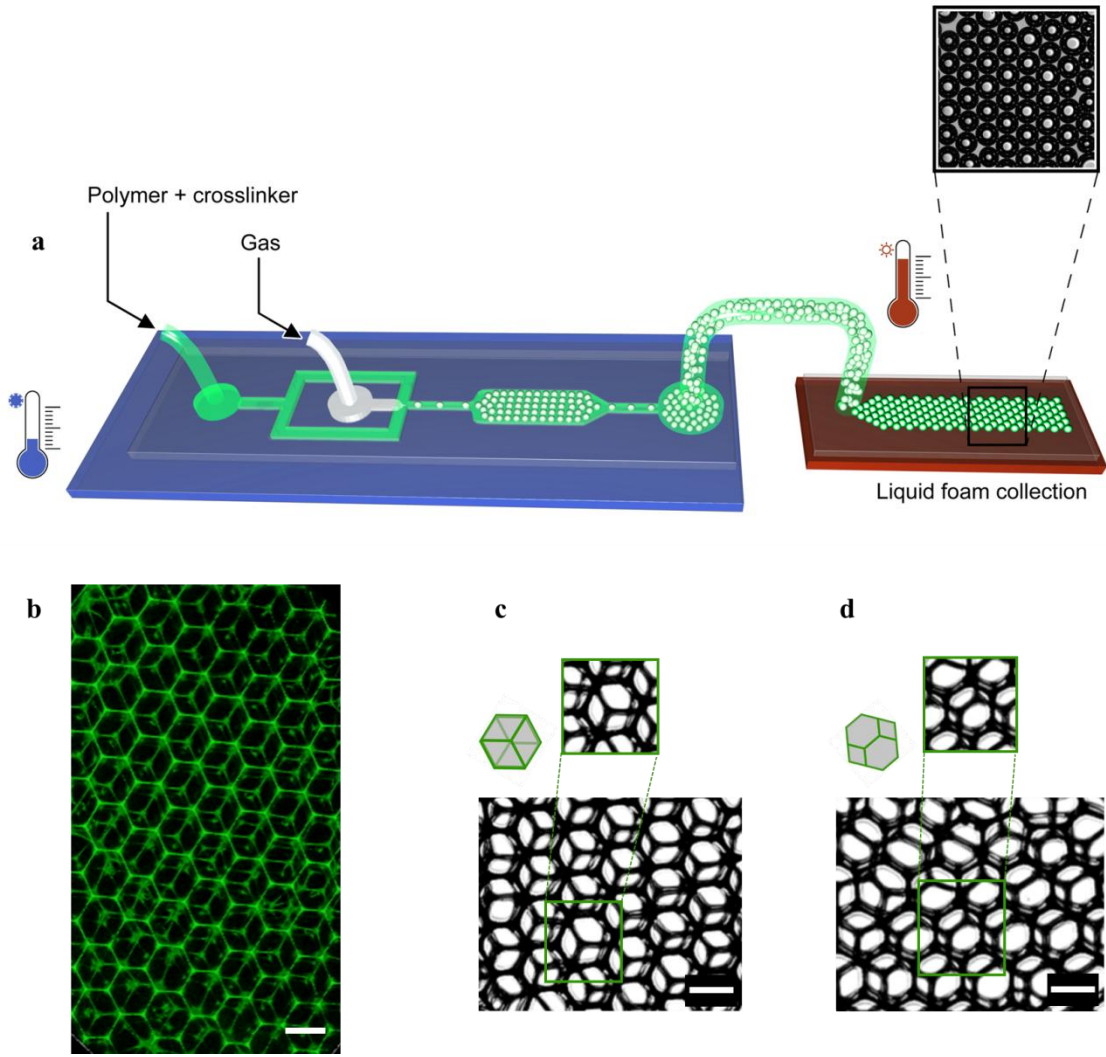


Figure 2

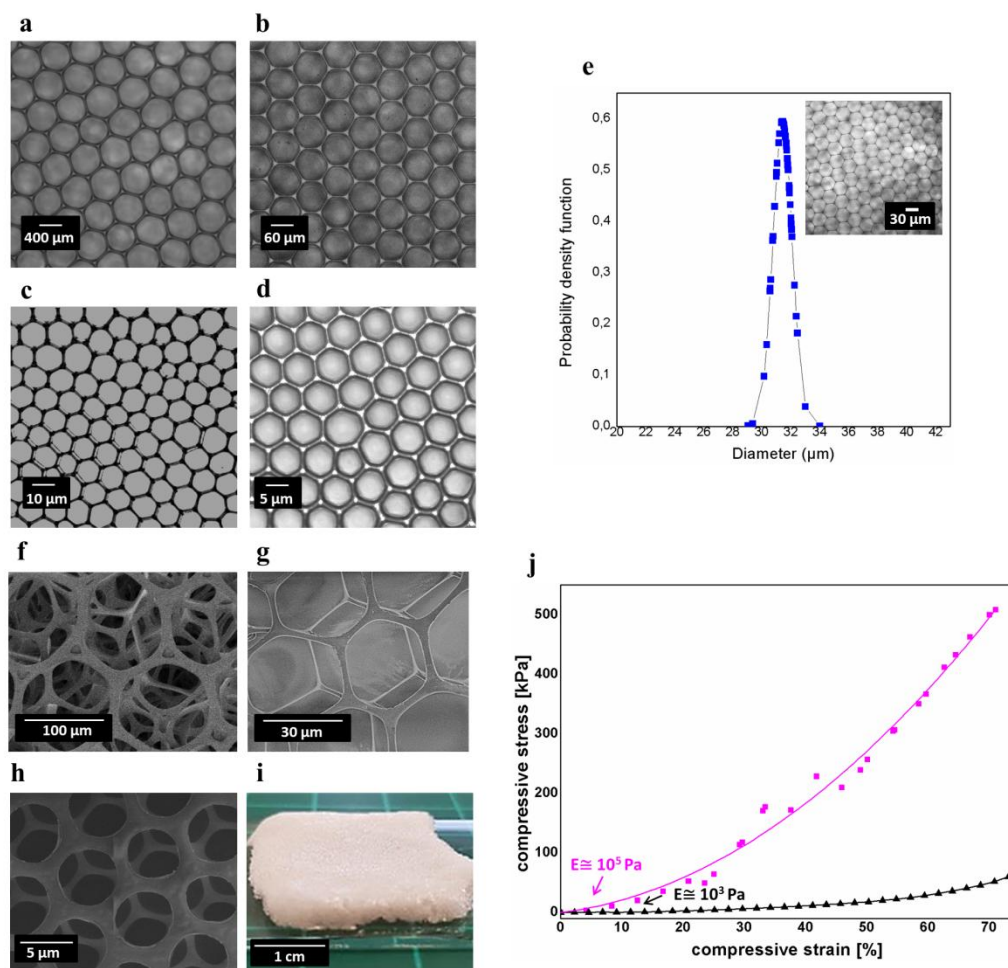


Figure 3.

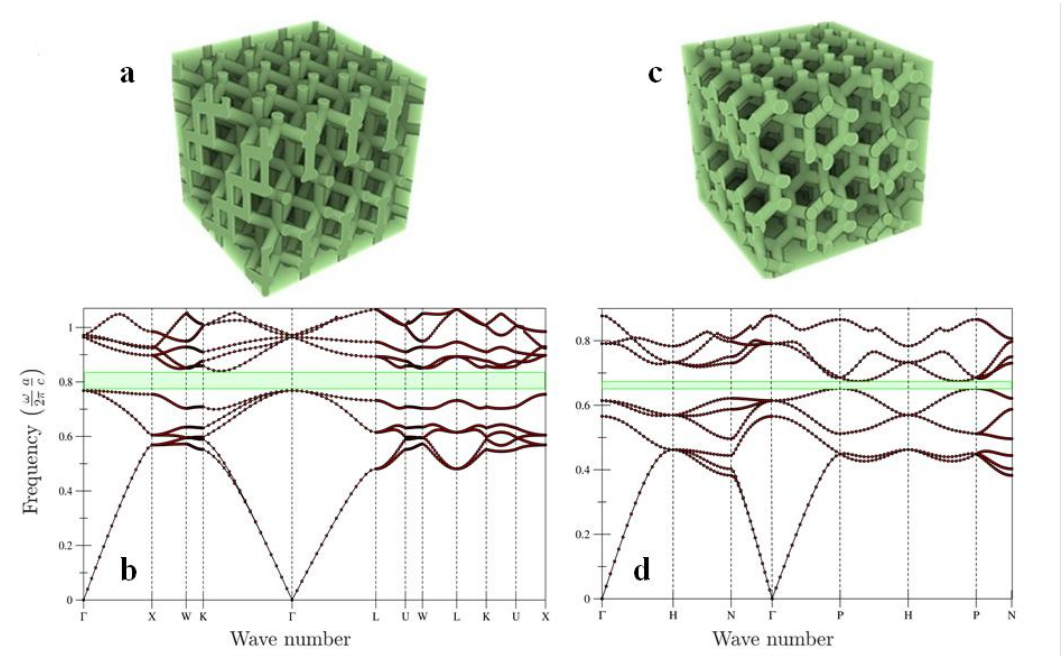
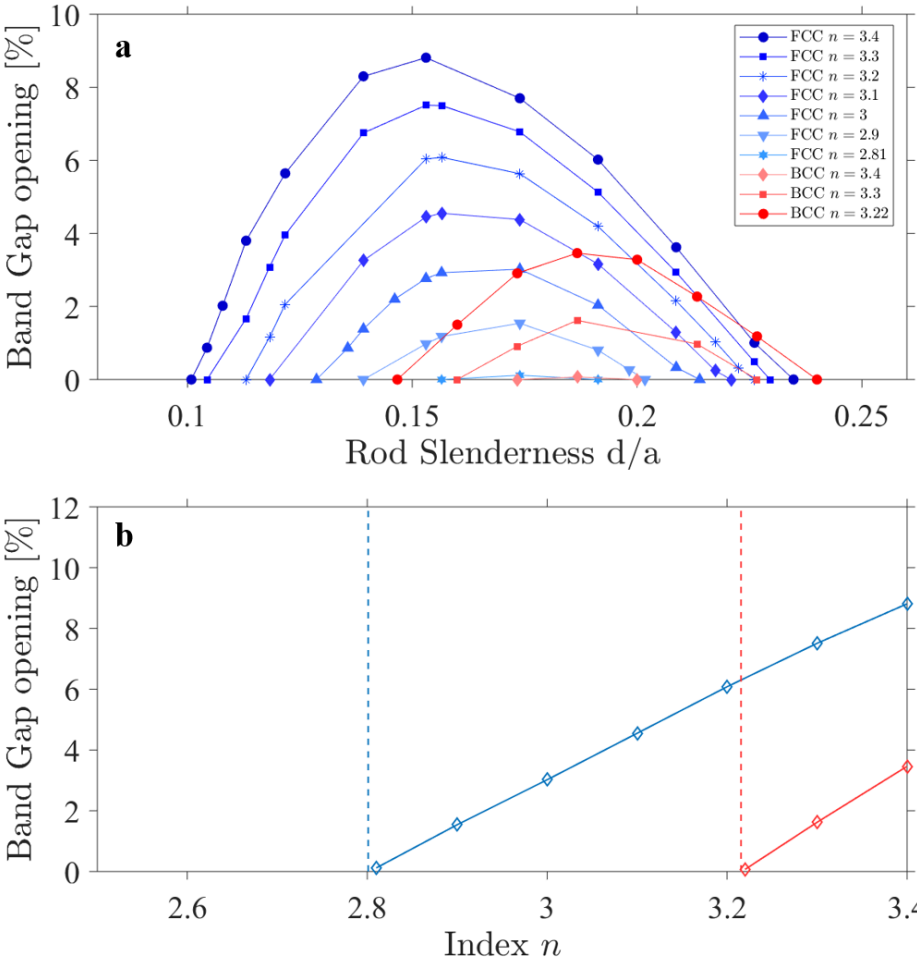


Figure 4.



**Figure 1. Experimental realization of tunable targeted foam structures.** **a** Experimental sketch of the Flow Focusing platform producing liquid foams – Inset of a liquid wet foam picture with characteristic roundish bubbles. **b** a typical 3D confocal reconstruction of the produced highly ordered open-cell solid foam with slender Plateau Borders of uniform thickness. Scale bar 100  $\mu\text{m}$ . **c** FCC chitosan solid foam (Filling fraction 11%, pore diameter: 20  $\mu\text{m}$ , Plateau border thickness  $\sim 11\mu\text{m}$ ). Scale bar 20  $\mu\text{m}$ . **d** BCC solid foam crystal domain in a coexisting BBC-FCC phase. Filling fraction 8%, pore diameter: 20  $\mu\text{m}$ , Plateau border thickness  $\sim 7\mu\text{m}$ ). Scale bar 20  $\mu\text{m}$ .

**Figure 2. Experimental scaling down and mechanical properties of the solid foam.** **a-d** Bright-field confocal images illustrating the pore size tuning between 400  $\mu\text{m}$  and 5  $\mu\text{m}$  with a narrow distribution. **e** The pores size distribution in **c** follows a Gaussian distribution, in the present case, centered around  $31\pm 0.6\ \mu\text{m}$  (Polydispersity index 2%); **f, g, h** SEM images of 3D solid foams with pore size ranging from 100  $\mu\text{m}$  to 5  $\mu\text{m}$ ; **i** photograph of a typical prepared solid foam sample; **j** compressive stress-strain curves of the foam sample (pore size of 100  $\mu\text{m}$ ) for two different cross-linker concentrations: at 100 $\mu\text{L}$  of glyoxal (- $\blacktriangle$ -) and polynomial interpolation at 400 $\mu\text{L}$  of glyoxal (- $\square$ -) for 1 mL of chitosan at 0.6% wt.

**Figure 3. Band structure calculations for the FCC and BCC structure.** **a** (respectively **c**) Schematic representation of the FCC structure (resp. BCC structure). **b** (resp. **d**) Band structure calculations FCC (resp. BCC) for the optimal structure comprising cylinders of diameter  $d/a = 0.153$  (resp.  $d/a = 0.202$ ) corresponding to a filling ratio of 20.24% (resp. 20.94%), of relative dielectric constant  $\epsilon = 11.56$  and a spatial mesh of 128x128x128. The structure displays a photonic band gap of 8.95% (resp. 3.35%) around a reduced central wave number  $a/\lambda = 0.80$  (resp.  $a/\lambda = 0.66$ ).

**Figure 4. Optimal geometry for photonic band gap opening.** **a** Numerical evolution of the gap-midgap ratio (%BG) with the dimensionless rod's diameter  $\tilde{d} = d/a$ . Red (resp. blue) colors refers to FCC (resp. BCC) structures. The darkening of the colors indicates larger optical indices  $n$ . **b** Numerical evolution of the geometrically optimal gap-midgap ratio (%BG) with the optical index of the rods. Vertical red (resp. blue) dashed line evidence the critical optical index  $n^* = 2.80$  (resp.  $n^* = 3.21$ ) to open a band in the FCC (resp. BCC) structure.