Macroporous Silica Foams Fabricated via Soft Colloid Templating

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1. Introduction

Homogeneous materials with well-defined and uniform pore sizes, low to moderate solid content, and a tailored local topology are attractive for a wide variety of applications. Foams are such materials that can provide unique mechanical strength, or serve as filters for gases and liquids. They can also interact strongly with acoustic waves, thermal radiation, or visible light. Plateau’s laws guarantee a local topology favorable for photonic networks with edges forming exclusively tetrahedral vertices, similar to diamond crystals.

Previous work on photonic materials focused mainly on assembly strategies for photonics-related applications and in particular on the quest for photonic crystals (PCs) with a full photonic bandgap (PBG). With about thirty percent solid content, sponge-like materials can be obtained by crystal self-assembly or disordered packing of spheres and subsequent inversion, that is, filling interparticle gaps with a foreign material and removing the template. Inverse photonic “opal” crystals and glasses (PGs) are well-known examples for this type of materials. Photonic crystal materials already have led to applications in sensing, light-harvesting and nano-photonic integrated circuits used in telecommunications. Pure and organic/inorganic hybrid microgel photonic colloidal crystals have been reported. Sphere packing, however, unavoidably leads to face-centered cubic (fcc) or body-centered cubic (bcc) crystal symmetries with inferior performance and unfavorable local topology. Recently, Pine and coworkers demonstrated the assembly of micron-sized colloids into a diamond lattice, using an intricate multi-step process based on DNA-functionalized colloidal spheres. This strategy is promising as it could ultimately lead to complete bandgap materials, as suggested by electromagnetic simulations.

Independently, recent numerical studies showed that computer designed, disordered, hyperuniform, and amorphous diamond networks can equally display PBGs. Amorphous materials may offer advantages over PCs due to their inherent isotropy, leading, for example, to non-iridescent structural colors and enable freeform waveguides. In particular, hyperuniform structures are interesting since they show vanishing density fluctuation on large length scales.
assemblies, the pores show local short-range order but remain disordered on longer length scales.

Clearly, the potential for disordered photonic materials is huge, but while such structures are readily created in silico on a computer, practical routes have proven less straightforward. A relatively successful technique for fabrication of such materials is advanced 3D direct laser writing lithography. However, direct laser writing is time consuming, its resolution is still limited to features that can be active in the infrared wavelength range and, moreover, postprocessing often leads to artifacts such as roughness and heterogeneous shrinking.

A second approach focuses on self-assembly on mesoscopic length scales. Klatt et al. and Ricouvier et al. suggested that ordered and disordered dry foam structures are promising candidates for PBG materials that might be obtained by self-organization, as their local topology resembles the fourfold symmetry found in diamond networks. Self-assembly of solid dry foams with uniform, submicron pore sizes is however highly challenging. Different structure-directing agents such as bacteria, bio-templates, polymer foams or emulsions have already been investigated. Classical polymer-based (like polystyrene) porous polyHIPE (polymers synthesized with high internal phase emulsions) materials are obtained using emulsion templates. Emulsion templating of silica has been reported via the interaction of silica precursor molecules at the droplet interface, forming a solid shell. The size of the emulsion droplets determines the size of the resulting pores, which can reach length scales comparable to optical wavelengths. The critical tradeoff for all aforementioned strategies generating (dis)ordered dry foams is between the well-defined spherical shape of the sacrificial building block and its compressibility. The former is crucial to obtain monodisperse pore sizes. At the same time, the latter is required to obtain a faceted pore shape under compression.

Although the template-assisted generation of dry foams with monodisperse pore size is demanding, they promise better photonic properties than the more traditional hard-sphere colloidal templated PGs or PCs. First, packings of spherical particles or droplets, or their inverse counterparts, do not show robust PBGs, even at high refractive indexes. Direct opals (fcc lattice) as well as randomly packed (rcp) assemblies of spheres do not display a bandgap. Inverted rcp-close packed (rcp) assemblies of spheres do not display a bandgap either. Such uniform tetrahedral coordination is favorable for the opening of a band gap as suggested by Weaire and Thorpe. A (foam-like) template with a diamond like uniform local topology could be achieved by templating with highly compressed emulsions or foams. At a droplet volume fraction of about 85%, droplets deform and develop facets, interstitial volumes would form plateau borders and a network of junctions, characteristic of a dry foam. The tetrahedral local topology would thus resemble similar hyperuniform networks that can also show complete bandgaps. Inverting such obtained structures with a high index material would thus result in lightweight networks with a filling fraction of 15% or less that could be later back-filled with the same material. Optimized volume filling fractions, with largest bandgaps, are usually found around 25%.

While feasible in principle, compressed emulsion templating of optical materials has not been explored successfully to date in 3D, likely due to challenges preparing monodisperse small droplets with sizes in the range of hundreds of nanometers, the high Laplace pressure of small droplets, as well as coalescence under compression. Recognizing the potential of dry foams as photonic materials, we propose herein a different solution toward preparation of solid, uniform, macroporous silica foams with monodisperse pore size yet faceted pore shape, using microgels as a size-tunable and mechanically soft colloidal template.

We take advantage of the fact that microgel colloids combine the thermoresponsive features of polymers, the spherically contained shape of solid colloidal particles, and the deformability of emulsion droplets. Our microgels are miniature hydrogels, which swell when lowering the temperature below the lower critical solution temperature of the polymer, T \text{LCT} ≈ 32°C. As shown in a recent superresolution microscopy study, at high effective volume fractions, the microgels start developing facets, thus resembling the pores in a dry foam. We decorated the microgel particles with ≈10 nm sized silica nanoparticles (NPs) and used their temperature-driven swelling properties to create disordered macroporous silica dry-foam structures by self-assembly. Once the silica foam is formed, we remove the polymer component by calcination, resulting in a pure silica foam-like structure.

We demonstrate that deformable microgel colloids can bridge the gap between colloidal and emulsion templating, facilitating the formation of disordered solid structures with uniform sub-micrometer pore sizes and the desired dry-foam topology.

2. Results

2.1. Synthesis of Silica Decorated Microgels

The design of the templating colloidal system was carefully selected towards its subsequent processing by sintering into inorganic foams. We prepared thermosensitive microgels and carried out self-assembly of silica nanoparticles into a dense coating shell. The microgel particles are made of polymer networks, grown by crosslinking the thermosensitive monomer N-isopropylacrylamide (NIPAM) together with a crosslinker, N, N’-methylenebis(acrylamide) (BIS), upon addition of an initiator. We adapted the starved feed batch-procedure described by Still et al., which results in the synthesis of microgel particles with homogeneous crosslinking. Toward the end of the synthesis, two additional ingredients were added into the feed: a small amount of the ionic comonomer N-(3-aminopropyl)methacrylamide hydrochloride (APMA) and commercially available silica nanoparticles (LUDOX AS-30 or AS-40). Electrostatic interactions with the charged comonomer allowed us to incorporate the negatively-charged nanoparticles into the periphery of the microgel network, thereby forming a uniform and dense coating layer.

Figure 1, a,b (see Experimental Section for more details). We do not control the exact amount of silica particles attached to the microgels and the most important parameter here is the monomer/silica ratio. If silica is added in excess, the excess amount will not bind to the microgels once the microgel/silica hybrid available binding sites
are saturated. Most of the excess silica can be readily removed in the purification process. To evaluate the effect of synthesis conditions and particle architecture on the final foam structure, we prepared two types of silica-decorated microgels. In the first synthesis (termed M1), we combine 5 mol% BIS-crosslinked microgels with Ludox AS-30 nanoparticles ($R = 6$ nm, 30 wt% concentration) with a silica:monomer weight ratio $\approx 1:10:1$. In the second synthesis (referred to as M2), we synthesized softer and larger microgels, by using 1.5 mol% BIS-crosslinker, paired with Ludox AS-40 NPs ($R = 13$ nm, 40 wt% concentration) with a silica:monomer weight ratio $= 0.3:1$. These design choices were made to ensure that microgels in M1 are smaller and stiffer, comprising a larger silica content, as compared to M2.

Microgel colloids were characterized as dilute suspensions by dynamic light scattering (DLS), as well as in the dry state, by scanning electron microscopy (SEM). SEM images of individual particles illustrate the decoration of microgel cores with a continuous shell of silica nanoparticles (Figure 1a,b). The hydrodynamic radii $R_H$ were determined by DLS, over a temperature range of 20–40 °C. Average values of $R_H = 256$ and 493 nm were determined at 20 °C for M1 and M2, respectively. The DLS results additionally confirmed that the microgels retain their thermoresponsive properties after coating with the silica NP-shell. Below the lower critical solution temperature (LCST) of about 32 °C, the microgel-polymer is in a good solvent and therefore in the swollen state. At temperatures above 32 °C, the microgel network expels the aqueous solvent, thereby resulting in more compact colloidal particles (Figure 1c). The stiffer character of microgel M1, due to its higher crosslinker content, is reflected in a more limited swelling, as compared to microgel M2, which was found to swell by almost a factor of 2 in radius. The particle radii at different temperatures are given in Figure 1. The particles are fairly monodisperse. From a SEM image analysis we find, for M1, $R_{SEM} = 163 \pm 15$ nm and for M2, $R_{SEM} = 386 \pm 19$ nm. From a DLS second cumulant analysis we find a size polydispersity at $T = 20$ °C of $R_H = 256 \pm 51$ nm (polydispersity index, PDI $= 0.2$) for M1 and $R_H = 493 \pm 113$ nm (PDI $= 0.23$) for M2. The DLS polydispersity values are somewhat larger compared to the SEM results, which could be a measurement artifact due to weak aggregation. Additional analysis of static light scattering (SLS) data for M2 confirms the thermoresponsive behavior of the colloid and its monodispersity (Note S1, Supporting Information).

2.2. Solid Foam Preparation by Self-Assembly

We used silica NP-decorated microgels to prepare silica foam networks, by means of a tailored compression process. Our strategy is outlined in Figure 2. Starting with a silica NP-microgel suspension (Figure 2a), we centrifuged $\approx 0.5$ mL at 16,200 g for 5 min and then removed the supernatant carefully. Subsequently, the sample was heated up to 70 °C for 2 min, so that the microgels undergo a phase transition and expel water, resulting in compression of the polymer network and reduction of particle size. The hot liquid suspension was centrifuged again at 16,200 g for 5 min, the supernatant rapidly removed, and then the sample was left to cool down to room temperature. By cooling again below 32 °C, the polymer network exerts a swelling pressure and pulls in the interstitial water phase, thereby pushing the silica NP-shells into a cellular foam-like scaffold, made of faceted interfaces and interstitial volumes filled with silica NPs, as shown in Figure 2b. We find that the NP-network provides mechanical stability to the structure and, once formed, does not rely on the presence of the swollen microgel particle anymore. Upon drying the sample at 70 °C, the silica NPs form a solid cellular network while the microgel-polymer dries out leaving behind voids within the network (Figure 2c). The dry polymer density is $\approx 1.1$ g mL$^{-1}$, a density much higher than the hydrated microgel–polymer (roughly 0.2–0.3 g mL$^{-1}$), thus about 70–80% of the volume occupied by the microgel is effectively replaced by air, forming the pores.

We characterized the dry silica-polymer monoliths by SEM, combined with focused ion beam (FIB) milling. FIB-milling is a technique, which uses a gallium ion beam to ablate sample material in thin layers with high spatial resolution. The use of the FIB instrument allowed us to reconstruct the 3D network into high-resolution tomography, which enabled us to investigate the internal structure of the monolith. We find that the compressed particles form a continuous solid macroporous network, as suggested in Figure 2c.
Figure 2. Strategy for the preparation of macroporous silica-foams. The microgel–polymer phase is labeled in blue while the silica NP-corona is labeled in red color. We proceed as follows: a) Suspension of NP-decorated microgels at 20 °C functions as starting material. b) Jamming of the microgel–silica hybrids by heating to 70 °C, centrifugation and subsequent reswelling at room temperature, thereby pushing the silica NPs to the flattened particle–particle interfaces. c) After drying, silica NPs form a solid silica network and the low-density microgel collapses onto the cell walls. d) Subsequent removal of the dry polymer by heat treatment (calcination) results in a lightweight pure silica cellular network with a foam-like structure and topology.

Figure 3. Characterization of network before calcination via alternation of focused ion beam (FIB) milling of thin slices and subsequent scanning electron microscopy (SEM) imaging (see also Figure 2c). Top row: typical 2D slices as obtained after FIB milling. The electron micrographs show the internal structure of macroporous foams obtained by using a) M1 and b) M2 microgels as templates. Bright areas correspond to the solid fraction (silica NPs and polymer), dark areas to air voids that were previously filled by the swollen microgel, as shown in Figure 2b. The inset sketches indicate the size of the different components of the microgel core–shell particles. Bottom row: 3D reconstruction from all 2D slices. The 3D-reconstruction reveals the internal structure of dried monoliths fabricated from samples c) M1 and d) M2. The size of the reconstructed regions for both samples was $2.5 \times 2.5 \times 2.5 \, \mu m$. 
Representative SEM 2D images of cross-sections imaged after FIB milling are shown in Figure 3a,b. Bright areas correspond to the solid fraction (silica NPs and polymer), whereas dark areas show the air-filled pores. Both M1 and M2 microgels yielded disordered solid foams with relatively monodisperse pore sizes and shapes. The obtained networks were found to be homogeneous throughout macroscopic sample volumes, with no apparent gradients. Note S2, Supporting Information, includes a SEM image of an entire monolith, as-obtained after drying. The monolith has a size of about 1 mm³ with an irregular shape.

Differences between the foam-like structures obtained for the two types of microgels are obvious and directly related to their design. Sample M1 (Figure 3a,c) features a high solid fraction with small spherical pores. In contrast, the solid silica/polymer network in monolith M2 (Figure 3b,d) comprises thinner walls, and the pores appear larger and more faceted. Quantitative image analysis (Figure 4) of the 3D tomographic FIB/SEM-reconstructions (Figure 3c,d) support these qualitative findings, see also Experimental Section. The calculated solid filling fraction (i.e., the volume occupied by the silica NPs and polymer) for monolith M1 is found to be between 74% and 84%, while only 47–54% for monolith M2. The measured filling fraction is determined by considering the ratio of white pixels to black pixels after binarization of the tomography, and therefore depends slightly on thresholding and smoothing of images. The measured pore radius distributions (Figure 4a) further illustrate the differences between using samples M1 and M2.

Mean pore radii of $54 \pm 7$ nm and $209 \pm 5$ nm were determined for monoliths M1 and M2, respectively, with a high degree of monodispersity =10%, comparable to the polydispersity of the primary particles. The pores are substantially smaller than the full hydrodynamic diameter of the microgel–silica hybrid particles. Several effects contribute to this difference: i) the presence of the silica corona, ii) the compression of the microgel core, iii) the coating with the dry polymer (Figure 2c).

An analysis of the pore sphericity $\psi = \frac{\pi^{1/3}(6V^{2/3})}{A}$ (with V the pore volume and A its surface area) and its distribution (Figure 4b) shows a peak slightly shifted toward values lower than one for both M1 and M2, as well as a significant fraction of pores with sphericity values around 0.90–0.95 in the case of M2. In the literature, the sphericity of perfect dry foams has been studied numerically using Surface Evolver.[44] Typically, for monodisperse random or ordered foams, the sphericity lies in the range 0.9–0.92. The sphericity is closely related to the common “surface free energy density” $E = \frac{(36\pi^{1/3})}{\psi}$, a fundamental property of foams often assessed in simulations. $E$ ranges from $(36\pi^{1/3}) = 4.836$ (spheres) to about 6 (for cubes).[45] Taking the mean value, we obtained $E = 4.99$ and 5.06 for M1 and M2, respectively. The decreased sphericity of the cells or pores indicates a faceted local topology, which is also supported by visual observation of the reconstructed images. Faceting is facilitated by the low crosslinker content in the “softer” colloid M2, in conjunction with a larger particle size.

**Figure 4.** Quantitative analysis of 3D tomographies shown in Figure 3c,d. a) Pore radius distribution for both types of microgels, M1 and M2. Mean values are $R_{\text{pore}} = 54 \pm 7$ nm (PDI = 0.13) for M1 and $209 \pm 5$ nm for M2 (PDI = 0.02), substantially smaller than the full hydrodynamic radius of the microgel–silica particles at $T = 20 \, ^\circ\text{C}$, see also Figure 1c. b) Pore sphericity for both types of microgels. Mean values are indicated. c) Pair-correlation functions of pores’ centers for structures fabricated using samples M1 and M2, showing pore center-center distances of $D = 174$ nm and $D = 460$ nm, respectively. d) Structure factors for the centers of pores in monolith structures. The reciprocal vectors $q$ were normalized using mean pore center–center distances extracted from the peaks of the pair-correlation functions (c). Due to the finite size of the reconstruction volume, data are truncated at low $q$-values.
We additionally calculated the pair correlation and structure functions, as shown in Figure 4c and described in Note S3, Supporting Information. As expected, a pronounced short-range order was found. The center-to-center distance $D$ suggests that microgel–silica particles are compressed by more than a factor of two in size, from a mean distance of kissing particles of $2R_{H1} = 512$ to $D = 174$ nm for M1 and $2R_{H2} = 986$ nm to $D = 460$ nm for M2. The sharp drop of the structure factor $S(q)$ for $qD/2\pi \leq 1$ suggests that, on large length scales, the samples can be classified as uniform or even hyperuniform, which is an important criterion toward achieving a strong photonic response in crystalline or amorphous dielectric materials (Figure 4d).

Our results clearly demonstrate the formation of disordered silica foams with uniform pore sizes, from soft colloid templates. Tailor-made particles M1 and M2 lead to different foam structures, highlighting the versatility of this fabrication method, which offers further potential toward nanoengineering materials with specific properties.

In a final step, we remove the polymer component by heat treatment. Samples were calcined at 550 °C for 10 h, which resulted in removal of the organic material (polymer) from the sample, see also Figure 2d. We confirmed the full decomposition of the polymer component using thermogravimetric analysis (TGA) (for details see Note S4, Supporting Information). TGA also allows us to determine experimentally the polymer and silica mass ratios in the self-assembled and dried templates (see Figure 2c). The silica mass ratios are 35% in the dry sample M1 and 29% in M2. We can now calculate the global silica volume fraction of the pure silica macroporous foam as obtained after calcination, using the assumptions that i) the calcination process leads to a complete sintering/densification of the silica phase (density of pure silica is 2.2 g mL$^{-1}$), and ii) full removal of the polymer occurs during calcination (see also Note S4, Supporting Information). We thus obtain $\phi_{M1} \approx 17 \pm 1\%$ and $\phi_{M2} \approx 9 \pm 0.5\%$, confirming the creation of a dry foam. In reality, the silica phase likely remains somewhat porous, thereby increasing the actual volume fraction occupied by the silica-network.

Calcination did not cause visible shrinking of the foam-like structure, which also remained intact (Figure 5). Calcination, however, exacerbates the consequences of using different primary particles M1 and M2. When using small and rigid particles and a higher silica content (M1), a stable more cellular network was obtained, which did not change noticeably in appearance, compared to the precursor network. In contrast, the network created from M2 has a lower silica content and was not so robust. Although 3D tomography indicates a closed-cell structure for noncalcined networks, after calcination we observe both perforated cell walls (Figure 5b,c and Note S5, Supporting Information) as well as some areas of the monolith.

**Figure 5.** Calcined pure silica networks prepared using larger M2 core–shell microgels (see Figure 2d). Bright areas indicate silica while dark areas show empty space. a–c) Scanning electron micrographs of a selected area with a cellular structure. The latter is revealed by FIB milling and tilted imaging (tilt 52°). A top view (a) and a zoom on a central part of the image (b) are shown. d) Top view of another sample area. e,f) Micrographs of sample interior (revealed by FIB-milling and tilted imaging) where cell walls had ruptured during calcination, resulting in a network structure. All scale bars are 2 μm.
where entire cell walls collapsed, revealing the network structure (Figure 5e, f). A finer control over this process would open a pathway toward the efficient fabrication of ordered and disordered foam-like networks of connected rods, as suggested by Ricouvier et al.\cite{13} and Klatt et al.\cite{6}

Our strategy opens up avenues for optical materials design for designer materials with a low density and highly controlled pore size and shape. The known magnesiothermic reduction process should also make it possible to convert the silicate networks into pure high refractive index silicon networks in just one more processing step.\cite{21} The final silicon volume fraction can be increased by adding silicon via chemical vapor deposition as discussed in.\cite{26} The latter process is straightforward and fast.

To evaluate silicon-converted monoliths’ potential for PBG applications, we calculate the band diagram for two different types of foam-derived structures based on a Weaire–Phelan foam crystal, similar to the approach proposed by Klatt et al.\cite{6}

First, we obtain an idealized (zero silicon volume fraction) Weaire–Phelan crystal using the Surface Evolver software.\cite{48}

Subsequently, we create a closed-cell structure with a chosen silicon volume fraction by assigning a finite thickness to the crystal cell walls (see Figure 6a for an illustration). Next, we derive realistic dry foams (5% silicon volume fraction) using Surface Evolver and we removed the cell walls between the bubbles to design open network structures. To increase the silicon volume fraction we homogeneously expand the remaining channels or struts (see Figure 6b). For the dielectric contrast $\varepsilon = 13$, or index contrast $n = \sqrt{\varepsilon} = 3.6$, we assume the same value as for bulk silicon in the near-infrared, for both cases.

The obtained structures have been discretized with a resolution of $128 \times 128 \times 128$ px. To calculate the photonic band structure, the MIT-MPB software was employed.\cite{49} A primitive cubic cell was chosen. The band structure in the common high-symmetry directions in the reciprocal space was calculated taking $10 \times k$ points in each direction. The tolerance of the MPB eigensolver was set to $10^{-4}$. First 100 bands were calculated for each structure. While the closed cell structure does not show a bandgap, the network structures indeed open a wide bandgap. Our results confirm earlier studies where the advantage of bicontinuous open-cell networks for opening a PBG was reported both for ordered and disordered systems.\cite{13, 18, 37, 50}

Based on these results, we can assume that, while monolith M1—which has a closed-cell appearance after calcination—will not open a bandgap, monolith M2 has a strong potential for opening one. Future work will require further investigation into optimizing pore size (with length scales corresponding to visible light wavelengths) and streamlining the preparation process to produce more homogeneous and regularly shaped monoliths, more suitable for spectral characterization and for evaluating potential applications, for example, in structural coloration.

3. Conclusions

Our results show that one can employ suspensions of tailor-made microgels decorated with silica to assemble monoliths with a silica foam structure. The compressed and reswollen microgel exerts pressure on the silica corona casting the NP-coated particles into the desired cellular shape and structure. The internal structure characterized by $g(r)$ or $S(q)$ is preserved during the drying and calcination steps. We can control the solid filling fraction by adapting the silica/polymer ratio, the degree of compression, and the microgel cores’ softness. Connecting the silica NPs via drying, we obtain a solid cellular structure that allows subsequent removal of the polymer phase by calcination. Moreover, we can tune foam properties, such as pore size and shape, by adjusting the size, crosslinker, and NP content by altering the microgel synthesis. We can further control the stability of the solid silica cellular foam during calcination by the amount of silica attached to the microgel particles during synthesis, which may lead to a controlled collapse of the cell walls. Our approach is versatile and robust. In addition to photonic applications, we propose that such macroporous solid silica foams may be relevant to many other research areas, such as catalysis, insulation, or filtration.

4. Experimental Section

Synthesis: Previously reported procedures were adapted for the synthesis of silica-covered microgels.\cite{43, 44} All chemicals were purchased from Sigma-Aldrich and used as received.

For colloid type M1, N-isopropylacrylamide (NIPAM, 97%, 1.460 g) and $N, N'$-Methylenebis(acrylamide) (BIS, 99%, 0.103 g) were dissolved in 85 mL of H$_2$O in a three-necked flask equipped with a magnetic stirrer and a reflux condenser. Then, 5 mL of (N-(3-aminopropyl)methacrylamide

![Figure 6. Photonic band diagrams of a) closed-cell and b) network foam-like structures derived from a Wearie–Phelan crystalline foam. Cubic primitive cell with a lattice constant $a$ and a dielectric contrast $\varepsilon = 13$ at a volume filling fraction $\phi = 21\%$. Band diagrams $a/\lambda$, where $\lambda$ denotes the wavelength, obtained by the MPB-simulation package are shown on the left panel.](image)
hydrochloride (APMA, 98%) solution (6.6 mg in 10 mL H2O) was added and the reaction was left to degas under inert atmosphere for 40 min at room temperature. It was noted that the presence of the APMA comonomer allowed for further functionalization of the microgels and its tunability.[42] Next, the temperature was raised to 70 °C and 2,2'-azobis(2-methylpropionamide) dihydrochloride (AMPH, 98%, 0.0365 g in 5 mL H2O) was added. After 10 min, the solution turned from transparent to milky. At this time, another 5 mL of APMA solution was added, to incorporate the comonomer into the outer region of the microgels. Subsequently 39.89 mL of Ludox SM-30 colloidal silica (30 wt.% suspension in water) was added to the mixture. The reaction mixture was kept for 4 h at 70 °C and left to cool down overnight under continuous stirring. After the reaction was completed, the sample was purified by four centrifugation cycles at 11 200 g (30 min) followed by rinsing with deionized water.

For colloid type M2, NIPAM (5.6 g) and BIS (0.1162 g) were dissolved in 140 mL H2O in a three-necked flask (outfitted with a magnetic stirrer and a reflux condenser) and purged by bubbling with nitrogen for 20 min at room temperature while stirring (main solution). 50 mL of the main solution was mixed with 10 mL degassed H2O and filled in a syringe (portion 1). Another 50 mL of the main solution was mixed with 10 mL degassed H2O, APMA (0.00792 g), and Ludox AS-40 colloidal silica solution (40 wt% suspension in water, 4.5 g) and filled in a syringe (portion 2). The temperature of the remaining main solution was increased to 80 °C and left to stabilize for 10 min under degassing conditions. The N2 outlet was then placed above the surface of the main solution to avoid foam formation. To start the reaction, the initiator potassium persulfate (KPS, 99%, 10.4 mg in 2 mL H2O) was added to the main solution. Once the main solution turned white (4 min after initiator addition), 50 mL of portion 1 and 50 mL of portion 2 were consecutively fed into the main solution via a syringe pump (rate: 1 mL min⁻¹). After addition of portion 2, the main solution was left for 5 min before being placed in an ice bath. After filtration the sample was purified by three centrifugation cycles at 15 000 g (30 min) followed by rinsing with deionized water. It was noted that the synthesis procedures for M1 and M2 were slightly different which may affect their final structure.

Sample Preparation: An Eppendorf tube containing 1 mL of M1 or M2 suspension was centrifuged at 16 200 g for 5 min and subsequently the supernatant was removed. The sample was then placed in an oven at 70 °C for 2 min to induce the microgel deswelling. Next, the sample was immediately centrifuged (16 200 g for 5 min) at room temperature and immediately afterward supernatant was removed again. The goal of the current study was to prepare a sample of highly compressed microgel colloids covered with silica using a simple and rapid process. The thermal swelling and densification were not independently controlled by centrifugation, which something is planned to be done in a future work. The resulting monolith was placed on a SEM holder coated with silver paste and left to dry in the oven at 70 °C. After SEM characterization, the sample was calcined. The sample was heated to 30 °C (1 °C min⁻¹) and left for 6 h, followed by a heat ramp to 550 °C (50 °C h⁻¹) sustained for 10 h. Calcination was carried out in an open tubular oven and the sample was slowly cooled down inside the oven to avoid structural stress. The sample was then imaged with SEM again.

Light Scattering: For light scattering analysis an NMR-tube filled with a dilute suspension of 2 μL stock solution plus 200 μL deionized water was placed inside a 3D-DLS light scattering spectrometer (LS Instruments, Switzerland) operating at a laser wavelength 660 nm. The scattered intensity was collected from 20–40 °C in 3D-cross correlation mode which suppresses multiple scattering at angles 30–140° with step size 3°. Three measurements were obtained at each angle with duration 60 s. The hydrodynamic radius (and corresponding PDI) was calculated via a standard second cumulant fit on the auto-correlation functions of pores' centers as explained in Note S4, Supporting Information in more detail.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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