chanical hysteresis cycles of stretching and relaxation were performed on the stress-relaxed fibers. In these cycles fibers with a new initial length L_r were stretched up to the final length $L_f = 6 L_0$, i.e., up to the elongation $\varepsilon = [(L_f - L_r)/L_r] \times 100$, and then relaxed at controlled rate.

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Directed Self-Assembly of Spherical Particles on Patterned Electrodes by an Applied Electric Field**

By *Adam Winkleman, Byron D. Gates, Logan S. McCarty*, and *George M. Whitesides**

This manuscript describes a process in which glass microspheres with a 100 μm diameter self-assemble on a patterned electrode under the influence of an applied electric field. We have demonstrated that this process occurs for ordered arrays and arbitrary patterns, over areas up to ~0.7 cm^2, with a defect rate (e.g., missing spheres or extra spheres) of about 1 %. These arrays of microspheres on the surface of the electrode can be transferred into polymeric matrices, such as polydi-

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methylsiloxane (PDMS), polyurethane (e.g., NOA 65), and epoxy (e.g., SU-8). This method employs reusable templates to guide components rapidly (< 5 s) into ordered structures that cannot be made by traditional lithographic techniques.

Self-Assembly: Self-assembly can distribute small, preformed components into desired patterns. Methods now commonly used for assembling such components (i.e., pick-and-place robotics) can be costly and slow when compared to self-assembly; the advantages of self-assembly will become more pronounced as the size of the components continues to decrease. Self-assembly also can fabricate structures (e.g., arrays of spheres) that are not accessible to traditional photolithographic techniques.[1,2]

Non-Templated Electrostatic Self-Assembly: Self-assembly can use many types of forces (including the electrostatic forces important in this work) to order arrays of spherical particles.[3] Tribocharging, or contact electrification, has yielded regular, two-dimensional (2D) lattices of millimeter-sized polymeric spheres with charges of opposite types.[4] Fabrication of photonic materials, including photonic-bandgap crystals and waveguides, has driven the research in this field. Electrophoresis-enhanced gravitational sedimentation,[5] alternating-current fields perpendicular to gravitational sedimentation,[6–9] two- and three- dimensional electrohydrodynamic crystallization,[10,11] and electrodeposition of charged particles on electrodes[12] are all methods that employ external electric fields to drive the assembly and crystallization of colloidal suspensions in fluids. In addition to electrostatic driving forces, capillary interactions[13–15] and gravitational sedimentation[16,17] have guided the assembly and crystallization of suspensions of micro- and nanoparticles. These techniques yield a limited subset of possible lattice structures, typically face-centered cubic or hexagonal closed-packed lattices, and usually provide little or no control over the interparticle lattice spacing. In addition, the rate of assembly—on the order of minutes to hours—is not practical for most applications.

Templated Self-Assembly: Templates permit the fabrication by self-assembly of structures not otherwise possible. There are three general approaches to templated self-assembly on substrates: i) patterned chemical modifications of the surface, ii) patterned charge, and iii) patterned topography. Patterned chemical modifications of the surface of the substrate result in preferential adsorption of particles to the selected regions.[18,19] Techniques involving patterned charge on the surface of the substrate include focused ion-beam irradiation,[20] microcontact printing of alkanethiols on gold,[21,22] selective adsorption of polyelectrolytes,[23,24] and electrostatic microcontact printing.[25,26] These methods have not assembled high-quality periodic, well-ordered lattices. Patterned topography of the substrate such as wells,[27,28] lithographically patterned reliefs,[29] or microfluidic channels[30] confine and control colloidal assemblies. By altering the ratio of the size of the particle to the size of the patterned feature, a variety of different lattices can be assembled.[28,30] Shape-selective reliefs have oriented and registered asymmetric particles into assembled lattices.[31] In addition, the combination of physical

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boundaries and external electric fields were used to decrease the defects and grain boundaries in assembled lattices.[32,33]

Description of the Process: Figures 1a–e outline the procedure we used to create the templated electrode; the spheres self-assembled electrostatically on this patterned electrode. We prepared the substrate by depositing an ~3 nm film of chromium on the surface of a polystyrene (PS) cell-culture Petri dish (where the surface of this dish has been oxidized by

Figure 1. A schematic representation of template-directed self-assembly of microspheres on a patterned gold electrode using an applied electric field. a,b) Microcontact printing and etching generated a templated electrode. c,d) Microspheres self-assembled over the templated electrodes when a –20 kV potential (relative to ground) was applied to the patterned gold electrode. During this process, the excess spheres were ejected from the surface of the electrode. e) Ideally, one microsphere remained on each window, with no microspheres on the gold surface. The two arrows indicate the two types of defects (i.e., a window with a missing microsphere, and an extra microsphere on the gold electrode). f) A typical large-area square lattice of assembled microspheres. Circles surround examples of both types of defects. In addition, misaligned spheres can be found in the array. We do not consider this type of misalignment to be an error, because they are due to irregular, non-spherical particles; the shape of these particles causes them to shift from the center of the window in which they rest.

the manufacturer to increase its polarity), followed by an ~45 nm film of gold. The Au/Cr/PS was patterned with a self-assembled monolayer (SAM) of 1-hexadecanethiol by microcontact printing.[34] Removing the regions of Au/Cr that were not protected by the SAM by etching with an aqueous ferricyanide/ferrocyanide solution generated a pattern of ~75 μm diameter circles (windows) of PS exposed in the gold sheet.[35] The resulting patterned gold electrode (dry) was covered with 1 to 10 layers of 100 μm diameter glass microspheres. The process for self-assembly was dry; no suspending liquid is involved. A –20 kV voltage relative to ground from a direct-current high-voltage power supply was applied for ~4 s to the gold electrode. We experimentally optimized the procedure to minimize the defect rate. Voltages as low as ~–10 kV would also cause the assembly to occur, but with higher defect rates. The substrate was manually agitated by gentle tapping. The exact amount and degree of agitation was determined optically with a stereoscope to ensure that it was sufficient to cause the excess spheres to be removed, but not so violent as to disrupt the correctly assembled spheres. Microspheres on the gold surface were repelled and ejected from the electrode, while spheres resting on the PS windows remained on the surface. To verify that the driving force for the assembly is an electrostatic interaction between the electrode and the spheres, we repeated the experiment without applying a potential to the patterned electrode. In this case, no assembly was observed. We infer that the electrostatic interactions drive the assembly, and the mechanical agitation minimizes the defect rate.
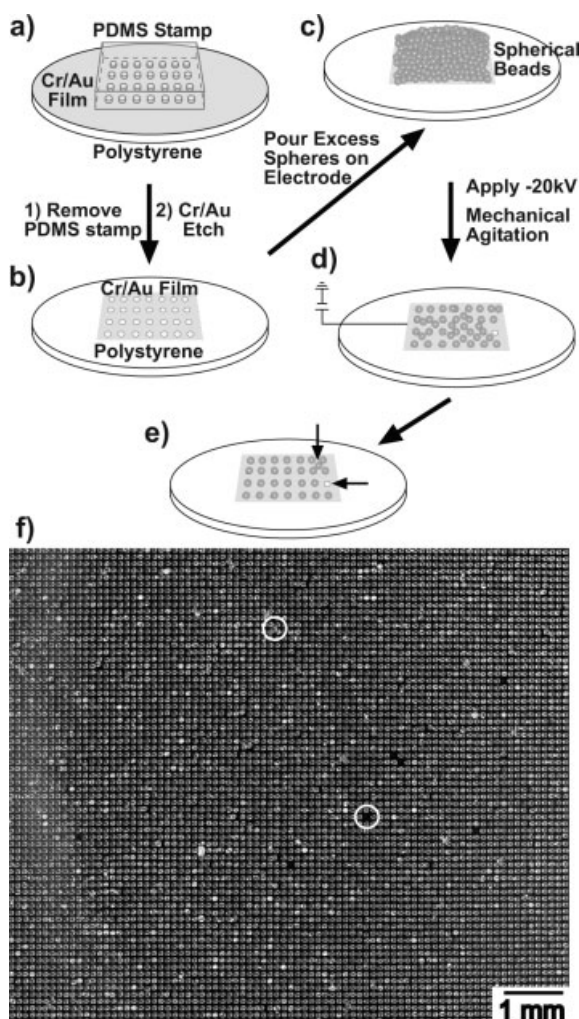
Defects: This method of templated self-assembly did not yield perfect arrays. The defect rate D (in percent) of our assemblies is defined as

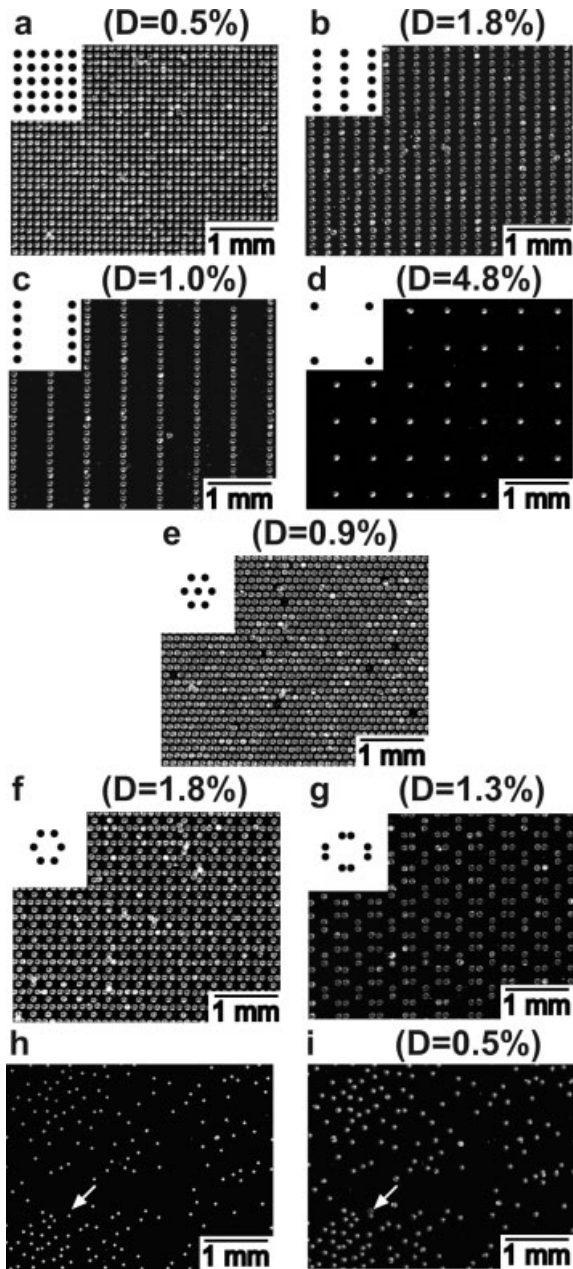$$D = (d/s) \times 100 \qquad (1)$$

where d is the number of defects and s is the number of sites. A defect is either an extra sphere in an unwanted location or a sphere missing from a desired site. Figure 1f is a typical example of a large-area array (~0.7 cm^2); this array contains 5810 lattice sites and only 32 defects (7 missing and 25 excess beads; examples of both types of defects are circled). The level of defects in self-assembly was thus 0.6 % in this example.

A complete mechanistic understanding of this process might enable us to improve the system and further minimize the number of defects. Currently, we are investigating possible mechanisms, both theoretically and experimentally.

Patterns of the Electrode: This method began with an electrode patterned into an array of windows; these windows reveal the PS substrate. The method could, in principle and in practice, use electrodes having a wide variety of patterns. The lattice of the exposed windows on the gold electrode determined the final structure of the assembled particles. Figures 2a–d show representative structures fabricated in a rectangular lattice. Figure 2e shows a closed hexagonal lattice, and Figures 2f,g show a pair of open-lattice structures. Figure 2h is an image of a Cr/Au electrode patterned with an

Figure 2. Optical microscopy images of 100 μm diameter glass spheres self-assembled over various patterns of PS windows on gold electrodes by an applied electric field. Six substrates are shown with patterned gold electrodes. a–d) The first four are rectangular lattices. Other patterns of e) a closed hexagonal lattice, f) a hexagonal lattice with periodic vacancies, and g) an open-lattice structure are shown. Images of h) the electrode of a random pattern of PS windows and i) the corresponding assembly. An arrow indicates the sole defect in the assembly (an excess sphere).

interactions between spheres are required for self-assembly. The assembly shown in Figure 2a was repeated ten times, and the average defect rate was 1.8±0.7 %; each assembly led to a different pattern of defects.

Although currently we only show the assembly of glass microspheres, preliminary results have demonstrated that this method can be applied to other dielectric materials (polystyrene microspheres), semiconductors (silicon particles), and metals (copper shot).

Transfer of Microsphere Arrays from the Electrode into PDMS: The arrays of microspheres, once assembled, could be transferred from the patterned PS/gold electrode into polymer matrices. In one procedure, we transferred the lattice array to a slab of partially cured and tacky PDMS backed by a piece of fully cured PDMS (Figs. 3a–c). This slab of PDMS was lowered, tacky-side down, onto the array without applying any external pressure, and then carefully removed vertically. The resulting PDMS slab with a lattice of adhering glass microspheres was placed in a 70 °C oven for ~10 min to complete the curing of the PDMS. Only about one quarter of each bead was embedded in the PDMS slab (Fig. 4a; the inset shows the optical diffraction pattern from the array).
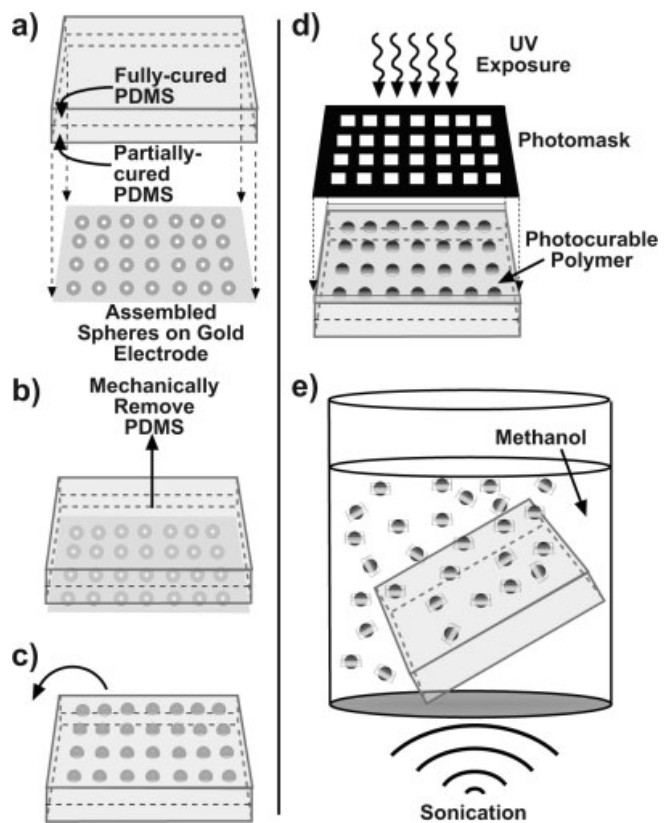
Figure 3. A schematic representation of the process used to transfer the assembled lattice of microspheres from the patterned, gold electrode into another polymer. a–c) The process used to transfer the glass spheres from the PS/gold electrode into a PDMS matrix. d,e) Photolithography of the embedded spheres and a photoactive polymer is used to fabricate new composite materials. These structures are subsequently released from the PDMS slab.

array of randomly placed windows. Figure 2i shows the assembly of spheres over the electrode shown in Figure 2h. The observation that self-assembly takes place on an array of windows with random locations suggests that the interactions responsible for assembly are local—involving only the electrode, the sphere, and the PS—and that neither symmetry nor
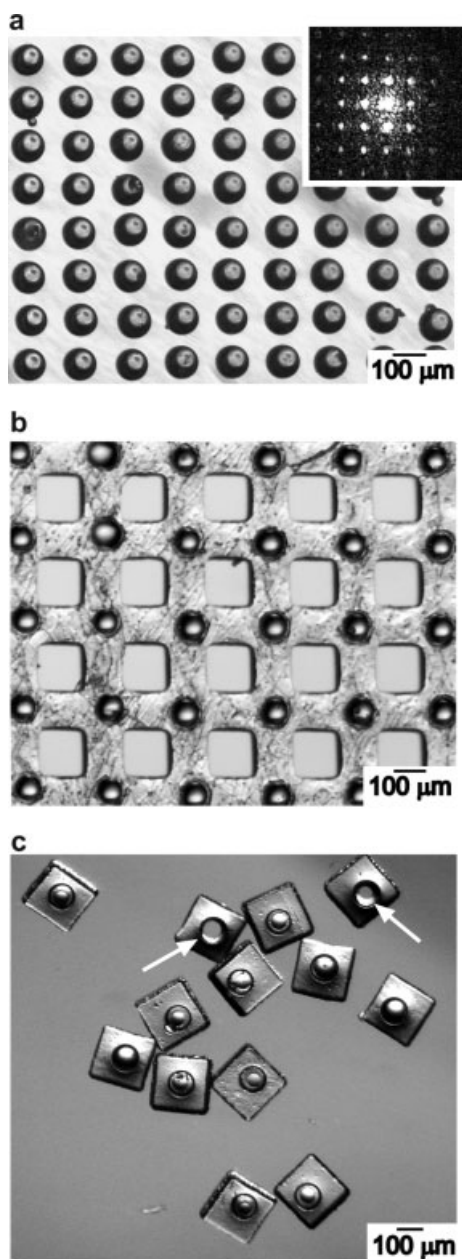
Figure 4. Optical microscopy images of 100 μm diameter glass spheres transferred from the PS/gold electrode into polymeric matrices. a) A square lattice of spheres was embedded in a solid slab of PDMS. The bright region on each microsphere is due to a reflection from the illuminating light on the microscope. The inset shows the diffraction pattern from a laser beam ($\lambda = 532$ nm) normal to the sphere–PDMS composite material. b) An open grid of polyurethane, with a single glass sphere at each grid intersection. c) Square pieces of SU-8 with one glass sphere partially embedded in the center of each square (Fig. 3e). The adhesion of glass to SU-8 is weak, and sonication dislodges some of the beads from the SU-8. Two pieces of polymer that have lost spheres are indicated by the white arrows.

Repeated Use of the Patterned Electrodes: After transferring the array of spheres to the PDMS slab, the PS/gold electrode can be reused. The array shown in Figure 4a was made from the fifth assembly of microspheres over the same electrode.

We have successfully used the same electrode at least twenty times without noticing any adverse effects to the accuracy of the assembly, so long as the electrode was washed with water followed by ethanol and dried between uses.

Transfer of Microsphere Array from PDMS to Photoactive Polymers: After the array of spheres was embedded in a PDMS block, it could be transferred again into a different polymer matrix, including matrices incompatible with the original PS/gold substrate. In two slightly different experiments of this type, we used a second polymer matrix that could be patterned using photolithography (Figs. 3d,e). After spin-coating either polyurethane or SU-8 onto the spheres partially embedded in PDMS, a photomask was aligned with the array and the system was exposed to UV light and developed using conventional multistep photolithographic methods. We released the final structures from the PDMS by soaking in methanol, and either peeling the membrane off mechanically or sonicating the solution for ~25 s. The resulting structure could be either a complex 2D composite of glass and polymer with the entire lattice structure remaining intact (Fig. 4b) or individual composite pieces where the lattice structure was used to align the spheres with the photomask (Fig. 4c).

Conclusions: This method for fabricating arbitrary, 2D lattices of microspheres uses electrostatic forces to drive self-assembly. It yields patterned arrays of spheres that can be transferred into other polymer structures, including those compatible with photolithography.

This system has three advantages relative to other techniques of self-assembly: i) The system is dry; it does not require a suspending liquid. ii) It is also rapid; relative to systems that rely on sedimentation or capillarity (e.g., Xia's templated fluidic system[27]), the rate of ordering—about 5 s—is at least a factor of a hundred faster than the hours to days required for those systems. iii) The method can produce arbitrary 2D arrangements of components. Properly patterned lithographic reliefs or wells could also fabricate similar lattice structures, but it would be more complex to transfer those patterns into other polymer matrices.

We have shown that the usefulness of this procedure, assembly of any arbitrary pattern of microspheres and transfer into a second polymer matrix, lies in its capability for rapid and repeatable fabrication of ordered arrays of particles which would be difficult or impossible to fabricate using conventional lithographic techniques.

This method also has three limitations: i) Each individual array is limited to a single particle type; AB-type lattices are not currently possible. Other methods are more versatile; Alien Technology's shape selectivity allows for the simultaneous assembly of multiple components with differing shapes.[36] ii) Most other methods can assemble spheres into three-dimensional (or at least multilayer) lattices, but this method is strictly limited to two dimensions. iii) We are not able to achieve perfect structures (the defect rate is about 1–2 %). It is difficult to compare this defect rate with that of other methods as there is not a standard method of reporting these rates.

Experimental

All materials and chemicals were purchased commercially and used as received.

Electrode Fabrication: Using previously reported methods, rapid-prototyping and soft-lithographic techniques were used to fabricate masters of SU-8 and subsequent stamps of polydimethylsiloxane (PDMS, Dow Corning, Sylgard 184) for microcontact printing [34]. Treated cell-culture dishes made of polystyrene (PS, Corning Inc.) were coated first with a film of chromium (~3 nm) to promote adhesion, and then with a film of gold (~45 nm) using an electron-beam evaporator. We patterned the gold-coated dish with 1-hexadecanethiol using an appropriate PDMS stamp. The unstamped regions of the Au/Cr surface were selectively etched by a solution of 1 M KOH, 0.1 M $Na_2S_2O_3$, 0.01 M $K_3Fe(CN)_6$, and 0.001 M $K_4Fe(CN)_6$ for ~20 min [35].

Electrostatic Assembly: The patterned PS/gold electrode was rinsed with water and ethanol before usage and only new beads were used to ensure that initially the system was electrically neutral. Glass spheres (100 μm diameter; Duke Scientific) were liberally poured over the patterned PS/gold electrode, and a voltage of –20 kV relative to ground was applied for ~4 s using a current-limiting power supply (Spellman CZE1000R) with the current limit set at ~25 μA. *Warning: use caution when working with these large voltages*. Simultaneously, the PS dish was mechanically agitated at a frequency of ~1 Hz by mechanically tapping the side of the dish.

Transfer of Assembled Spheres into PDMS: A ~2 mm thick PDMS slab was cured completely. Onto this slab, an additional 1–2 mm of PDMS was poured. This material was placed in an oven set to 70 °C to cure for ~30 min at which point the top surface remained slightly tacky. The tacky side of the 3–4 mm PDMS slab was manually lowered into contact with the assembled spheres on the electrode surface. The PDMS slab, containing the embedded microspheres, was lifted vertically from the electrode and placed into an oven set at 70 °C to complete the curing process of the tacky PDMS.

Transfer into Polyurethane: The embedded glass spheres in the PDMS slab were exposed to an oxidizing (air) plasma in a plasma cleaner (~266 Pa, 100 W, Harrick Scientific Model PDC-32G) for 1 min. The polyurethane (NOA-65, Norland Optical Adhesives) was spin-coated onto this oxidized surface at 500 rpm for 5 s and 750 rpm for 30 s. The transparency photomask was aligned with the lattice of spheres using an AB-M mask aligner. After bringing the mask into contact with the substrate, the sample was exposed to UV light for 7 s. The patterned composite was released by soaking the exposed sample in methanol at room temperature for one hour and mechanically separating the polyurethane/glass-microspheres structure from the PDMS slab using tweezers.

Transfer into SU-8: The embedded glass spheres in the PDMS slab were exposed to an oxidizing (air) plasma in a plasma cleaner (~266 Pa, 100 W, Harrick Scientific Model PDC-32G) for 1 min. SU-8 10 (MicroChem Corp.) was spin-coated onto the glass spheres embedded in PDMS at 500 rpm for 5 s and 1000 rpm for 30 s. The substrate was pre-baked at 75 °C for 2 min, ramped at +2 °C min⁻¹ to 105 °C, held at 105 °C for 5 min, and cooled at –2 °C min⁻¹ to 35 °C. The mask aligner was used to align a transparency photomask to the lattice of spheres, and the substrate was exposed to UV light for 8 s. The exposed sample was post-baked at 75 °C for 1 min, ramped at +2 °C min⁻¹ to 105 °C, held at 105 °C for 4 min, and cooled at –2 °C min⁻¹ to 35 °C. The sample was developed in 1-methoxy-2-propanol acetate (Aldrich Chemicals) for ~10 min to remove the uncrosslinked SU-8. The composite glass/SU-8 particles were released from the PDMS slab by sonication in methanol for ~25 s. The freely suspended glass/SU-8 pieces were isolated by either filtering the resulting suspension or evaporating the solvent.

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