

## Generation of a Library of Particles Having Controlled Sizes and Shapes via the Mechanical Elongation of Master Templates

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Herein we describe a versatile and readily scalable approach for the fabrication of particles with a variety of shapes and sizes from a single master template by augmenting the particle replication in nonwetting templates (PRINT) method with mechanical elongation. Repetition of the elongation steps in one direction leads to the fabrication of linear particles with high aspect ratio (AR), over 40 times greater than in the original master, while a range of particle shapes can be obtained by repeating the elongation procedure while changing the stretching direction, generating diamond, rectangular, curved parallelogram particles from a single cubic master.

### Introduction

Increasing efforts have been devoted to the development of fabrication methods that can be employed to produce colloidal particles with control of shape and aspect ratio (AR) for applications in a variety of fields such as microelectronics, photovoltaics, smart fluids, and drug delivery, among others.<sup>1–11</sup> The ability to scale up particle fabrication in an efficient and cost-effective manner is a crucial factor for the utility of any fabrication method, in addition to precise control of particle size and shape.<sup>12</sup> In soft-lithography based methods, a master template that has been prepared by traditional photolithographic techniques is used to define the size and shape of the depressions in the molds used for particle fabrication. While many elastomeric molds can be made from such a master template, the generation of new templates, an expensive and time-consuming step, is required to generate particles with different sizes or geometries.<sup>13</sup> Here we introduce a readily scalable approach for the fabrication of shape-specific particles based on the particle replication in nonwetting templates

(PRINT) method,<sup>14–19</sup> which can produce particles of many different sizes and shapes using the same master template. In our method, the features of the master template are replicated using an elastomeric material, which is mechanically stretched to elongate the features. The elongated features are then cast in a rigid material to generate a new master template, which is used to generate a nonwetting template from a photocurable perfluoropolyether (PFPE) for use in particle replication. Repetition of the elongation steps in one direction leads to the fabrication of linear particles with high AR, while a range of particle shapes can be obtained by repeating the elongation procedure while changing the stretching direction. Importantly, this method allows for the quick and inexpensive fabrication of particles with a variety of sizes and shapes from a single photolithographic master template.

### Experimental Section

**Materials and Instruments.** Elastomeric molds were made from poly(dimethyl siloxane) (PDMS, Dow Corning, Sylgard 184) composed of base and curing agent mixed in a 100:6 ratio. Both commercially available trimethyloylpropane ethoxylate triacrylate (PEGTA,  $M_w = 912$ ) and poly(ethylene glycol)-700-diacrylate (PEG<sub>700</sub>-DA) were purchased from Sigma-Aldrich and then filtered through alumina to remove inhibitor before use. Photocurable perfluoropolyether (Fluorocur, Liquidia Technologies) and  $\alpha$ -hydroxycyclohexyl phenylketone (HCPK, Sigma-Aldrich) were used as received. Scanning electron microscopy (SEM) images were captured on a Hitachi S-4700 instrument at a voltage of 2 KV. Computer simulation was done with LISA-Finite Element Technologies. The Young's modulus of PDMS was 0.43 MPa as determined by using an Instron model 5566 system. The Poisson's ratio of PDMS was 0.4.

**Fabrication of Elongated PFPE Molds.** Sylgard 184 base and curing agent were mixed and degassed under vacuum before application to patterned silicon wafers to a thickness of ~0.4 mm.

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- (1) Wang, Y.; Xu, H.; Zhang, X. *Adv. Mater.* **2009**, *21*, 2849–2864.  
(2) Lu, Y.; Yin, Y.; Xia, Y. *Adv. Mater.* **2001**, *13*, 415–420.  
(3) Wang, J.; Zhou, Y.; Yan, J.; Ding, L.; Ma, Y.; Cao, Y.; Wang, J.; Pei, J. *Chem. Mater.* **2009**, *21*, 2595–2597.  
(4) Champion, J.; Mitragotri, S. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 4930–4934.  
(5) Champion, J.; Katare, Y.; Mitragotri, S. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 11901–11904.  
(6) Martin, B.; Dermody, D.; Reiss, B.; Fang, M.; Lyon, L. A.; Natan, M.; Mallouk, T. *Adv. Mater.* **1999**, *11*, 1021–1025.  
(7) Park, S.; Lim, J.; Chung, S.; Mirkin, C. *Science* **2004**, *303*, 348–351.  
(8) Joanicot, M.; Ajdari, A. *Science* **2005**, *309*, 887–888.  
(9) Walther, A.; Müller, A. *Soft Matter* **2008**, *4*, 663–668.  
(10) Geng, Y.; Dalheimer, P.; Cai, S.; Tsai, R.; Tewari, M.; Minko, T.; Discher, D. *Nat. Nanotechnol.* **2007**, *2*, 249–255.  
(11) Wang, Y.; Han, P.; Xu, H.; Wang, Z.; Zhang, X.; Kabanov, A. *Langmuir* **2010**, *26*, 709–715.  
(12) Glotzer, S.; Solomon, M. *Nat. Mater.* **2007**, *6*, 557–562.  
(13) Merkel, T.; Herlihy, K.; Nunes, J.; Orgel, R.; Rolland, J.; DeSimone, J. *Langmuir* **2010**, *26*, 13086–13096.  
(14) Rolland, J.; Dam, R.; Schorzman, D.; Quake, S.; DeSimone, J. *J. Am. Chem. Soc.* **2004**, *126*, 2322–2323.  
(15) Rolland, J.; Hagberg, E.; Denison, G.; Carter, K.; DeSimone, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5796–5799.

- (16) Grattan, S.; Ropp, P.; Pohlhaus, P.; Luft, J.; Madden, V.; Napier, M.; DeSimone, J. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 11613–11618.  
(17) Brown, E.; Forman, N.; Orellana, C.; Zhang, H.; Maynor, B.; Betts, D.; DeSimone, J. *Nat. Mater.* **2010**, *9*, 220–224.  
(18) Kelly, J.; DeSimone, J. *J. Am. Chem. Soc.* **2008**, *130*, 5438–5439.  
(19) Zhang, H.; Nunes, J.; Grattan, S.; Herlihy, K.; Pohlhaus, P.; DeSimone, J. *New J. Phys.* **2009**, *11*, 075018.

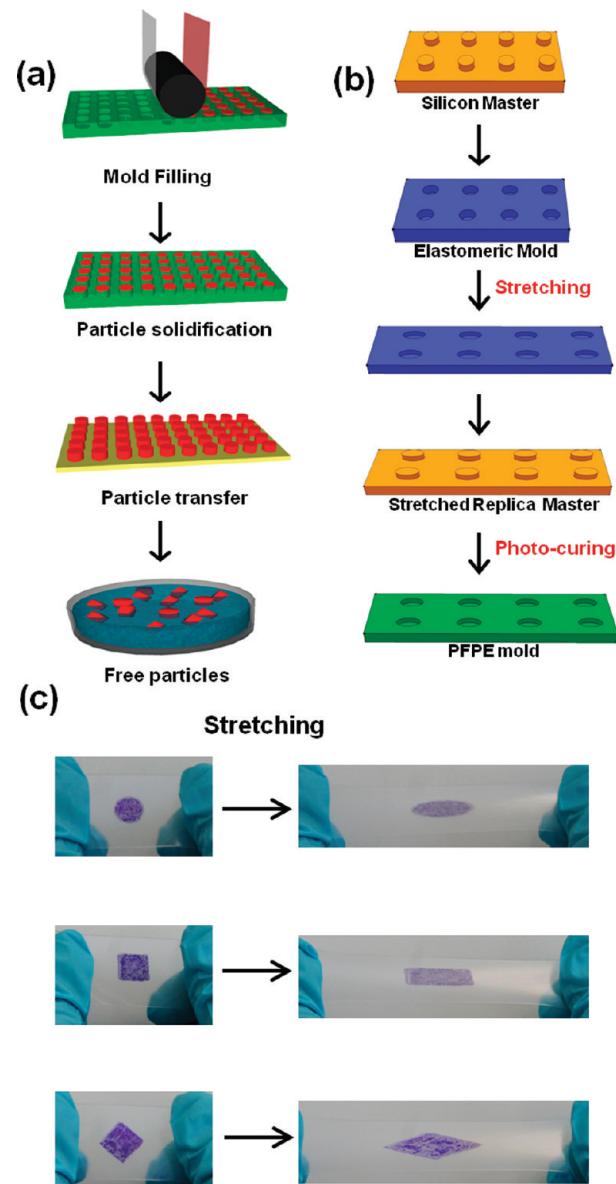
The PDMS was placed in an oven at 80 °C until it was cured, typically 1 h. After removing the PDMS molds from the patterned silicon wafer, the molds were elongated and held fixed at the desired state of extension. To fabricate a stretched replica master (SRM), 100 μL of PEGTA containing 0.2 wt % photoinitiator (HCPK) was drop cast onto the stretched elastomeric mold. The PEGTA and initiator were spread over the whole PDMS area with a sheet of poly(ethylene terephthalate) (PET). The assembly was placed into a UV oven and purged with dry nitrogen for 1 min, followed by 5 min of UV irradiation ( $\lambda = 365$  nm, power = 20 mW/cm<sup>2</sup>) to cure the PEGTA. Release of the PDMS from the cured PEGTA was followed by a relaxation of the tension from the stretched PDMS. PRINT molds were prepared from the SRM by application of 100 μL of PFPE resin with 0.2 wt % HCPK. A flexible plastic sheet was applied to the top of the resin to act as a supportive backing for the mold prior to photocuring. The resin was photocured for 5 min in a UV oven (as above) to produce a PFPE mold with elongated cavities. This PFPE mold was used to fabricate a new generation of particles via the PRINT process as described below.

**PRINT Technique for Particle Fabrication.** PEG<sub>700</sub>-DA was drop cast onto a PFPE mold, and a PET sheet was laminated to the top of the mold, wetting the total mold area. The sheet was peeled away at the nip point of a laminator, leaving the wells of the mold filled while wicking away excess solution. The filled PFPE mold was transferred to a nitrogen purged UV oven and cured with UV light for 3 min. The cured particles were transferred from the mold using a cyanoacrylate adhesive (PT08, ZAP). The adhesive layer was dissolved with acetone, yielding free-flowing particles. Excess adhesive was removed via centrifugation to pellet the particles, followed by removal of the supernatant and resuspension in acetone. These washing steps were repeated 5–10 times until no adhesive residue remained.

## Results and Discussion

In the PRINT process, as shown in Figure 1a, durable perfluoropolyether (PFPE) molds with size- and shape-specific cavities are replicated from a master template. Since PFPE molds exhibit nonwetting behavior and excellent compatibility to most liquid materials, the cavities are easily filled by liquid precursors to particles, including solutions of organic solvents, monomers, polymers, aqueous protein solutions, and others.<sup>13</sup> Once the liquid precursor to the particles fills the cavities via the PRINT process and is solidified, the array of particles can be removed from the mold onto a harvesting film. At this point, free-flowing particles can be obtained by separating the harvesting film from the particles. The well-defined master template, often produced by traditional photolithographic techniques, is of vital importance in determining the shape and size of particles generated via the PRINT process. Two factors, therefore, limit the adaptability and breadth of utility of PRINT: (1) the fabrication of each size and shape of particle requires the costly and time-intensive fabrication of a corresponding master template; (2) masters with high aspect ratio, or elongated, features can be expensive to make. The mechanical elongation strategy in this work addresses both issues, allowing many particle shapes, including those with high aspect ratio, to be fabricated from a common master template.

Fabrication of elongated PFPE molds begins with a patterned silicon master, which is used to generate an elastomeric mold with ordered cavities from an elastomer such as poly(dimethyl siloxane) (PDMS) (see Figure 1b). Once obtained, the patterned cavities on the PDMS mold can be systematically deformed in a variety of directions to generate elongated arrays, schematically illustrated in Figure 1c. Via this mechanical deformation, the lengths of the cavities increase parallel to the elongation direction while the width



**Figure 1.** Replication of elongated particles from mechanical elongation templates. (a) General schematic representation of particle replication in nonwetting templates (PRINT). The initial PFPE mold was replicated from a desirable master template. (b) Schematic illustration of the fabrication of elongated PFPE molds from mechanical elongation of a template. The relaxation of tension from the stretched replica master made of cured triacrylate-functionalized PEG. (c) Photographic images of elongated patterns, including circle to ellipse (top), square to rectangle (middle), and square to diamond (bottom).

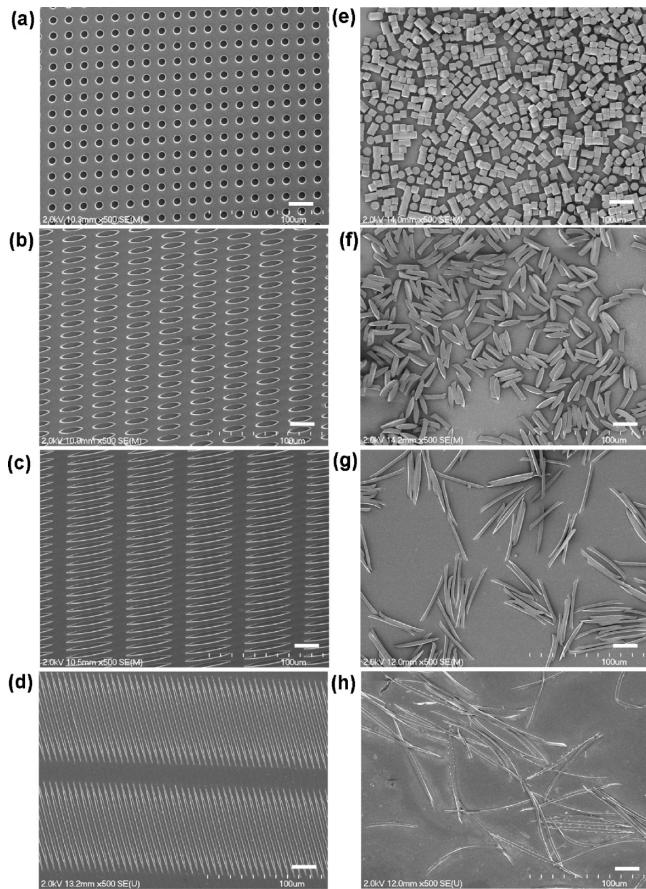
and thickness of the cavities decrease normal to the elongation direction.<sup>20–28</sup> Once the stretched mold is at the desired state of

- (21) Xia, Y.; Rogers, J.; Paul, K.; Whitesides, G. *Chem. Rev.* **1999**, *99*, 1823–1848.
- (22) Xia, Y.; Whitesides, G. *Langmuir* **1997**, *13*, 2059–2067.
- (23) Xia, Y.; Whitesides, G. *Adv. Mater.* **1995**, *7*, 471–473.
- (24) Pokroy, B.; Epstein, A.; Persson-Gulda, M.; Aizenberg, J. *Adv. Mater.* **2009**, *21*, 463–469.
- (25) Genzer, J.; Efimenko, K. *Science* **2000**, *290*, 2130–2133.
- (26) Russell, T. *Science* **2002**, *297*, 964–967.
- (27) Sun, Y.; Kumar, V.; Adesida, I.; Rogers, J. *Adv. Mater.* **2006**, *18*, 2857–2862.
- (28) Kim, D.-H.; Ahn, J.-H.; Choi, W. M.; Kim, H.-S.; Kim, T.-H.; Song, J.; Huang, Y.; Liu, Z.; Lu, C.; Rogers, J. *Science* **2008**, *320*, 507–511.

(20) Xia, Y.; Kim, E.; Zhao, X.-M.; Rogers, J.; Prentiss, M.; Whitesides, G. *Science* **1996**, *273*, 347–349.

extension, it is held at that state and is used to mold a new replica master from photocured triacrylate-functionalized poly(ethylene glycol) (PEGTA), a polar material from which the nonpolar PDMS and PFPE elastomers have excellent release properties. A layer of PFPE resin is then applied to the newly generated PEGTA stretched replica master (SRM) and is photocured to produce a PFPE mold with elongated cavities. This PFPE mold then is useful to generate a new generation of particles via the PRINT process as shown in Figure 1a.

The mechanical elongation strategy was utilized to make elongated molds and the corresponding particles, employing a silicon master template patterned with cylinders. Elastomeric

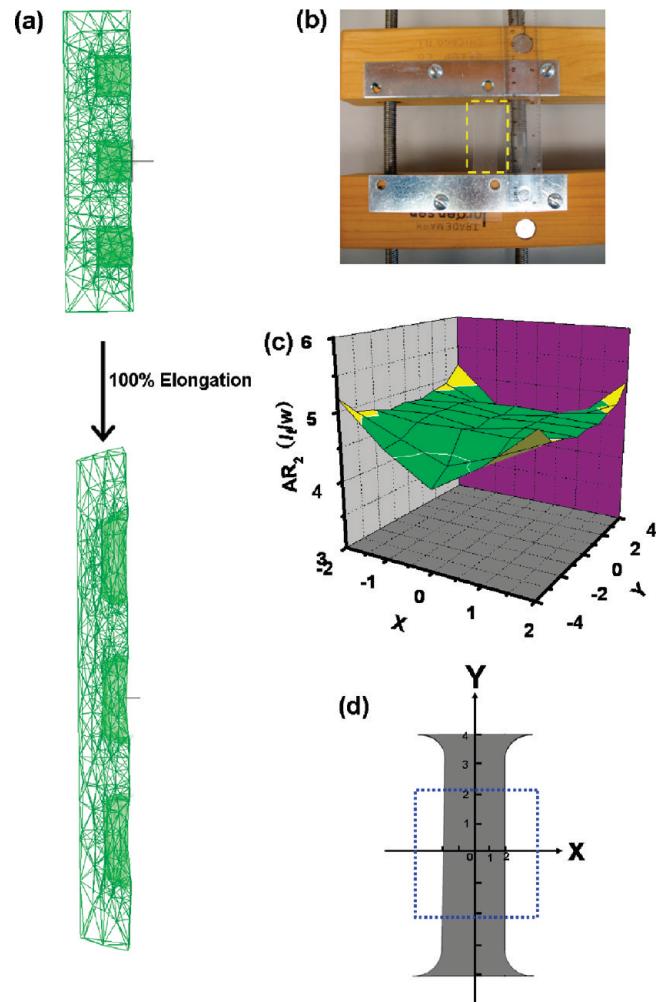


**Figure 2.** Fabrication of elongated well-bearing PFPE molds and corresponding PRINT particles from a cylindrical template. SEM images of (a) PFPE mold from the original cylindrical silicon master, (b) PFPE mold replicated from the first-generation stretched replica master (SRM), (c) PFPE mold replicated from second-generation SRM, (d) PFPE mold replicated from third-generation SRM. (e) Free cylindrical particles fabricated from the mold shown in (a). (f–h) Elongated particles fabricated from (b–d), respectively. Scale bar: 20  $\mu\text{m}$ .

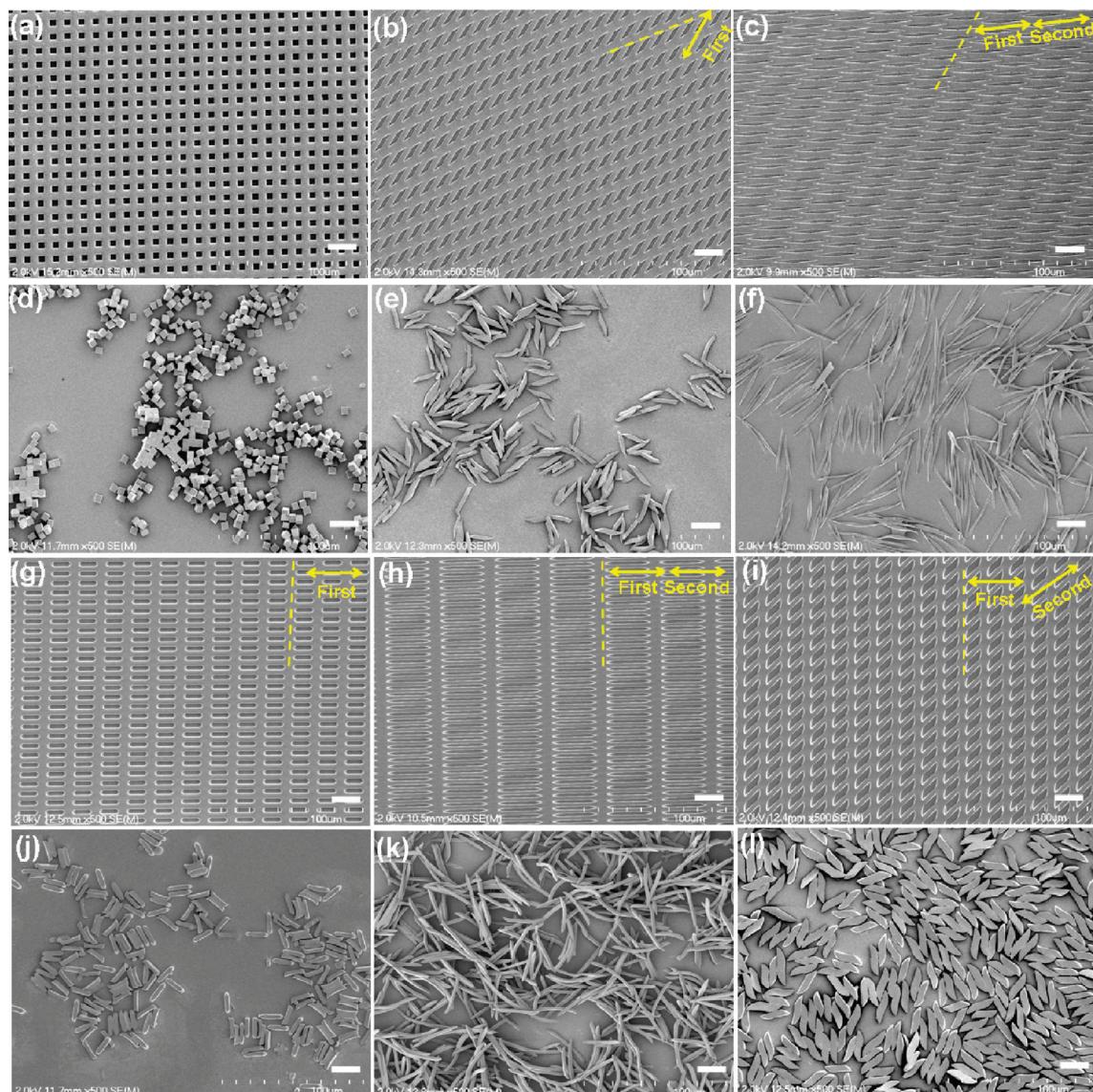
**Table 1.** Description of AR Change Examined by SEM Imaging after Each Generation of Mechanical Elongation, Where  $l_t$ ,  $w$ ,  $h$ , and  $l_b$  Are the Top Length, Width, Height, and Bottom Length, Respectively, of PRINT Particles Derived from Stretched Replica Masters

	$l_t$	$w$	$h$ ( $\mu\text{m}$ )	$w$ ( $\mu\text{m}$ )	$l_t$ ( $\mu\text{m}$ )	$l_b$ ( $\mu\text{m}$ )	$\text{AR}_1 (l_t/h)$	$\text{AR}_2 (l_t/w)$
Original Feature	$5.04 \pm 0.07$	$6.39 \pm 0.04$			$6.39 \pm 0.04$	$6.39 \pm 0.04$	1.27	1.00
First-Generation	$3.64 \pm 0.11$	$4.16 \pm 0.06$			$20.10 \pm 0.10$	$15.78 \pm 0.15$	5.52	4.83
Second-Generation	$2.20 \pm 0.08$	$3.05 \pm 0.05$			$39.84 \pm 0.17$	$31.46 \pm 0.23$	18.11	13.06
Third-Generation	$1.52 \pm 0.12$	$2.31 \pm 0.10$			$80.23 \pm 0.38$	$63.39 \pm 0.22$	52.78	34.73

molds with regular cylindrical cavities can be replicated straightforwardly using either PDMS or PFPE from the silicon master (Figure 2a). By following the mechanical elongation and replication process discussed above, a PFPE mold patterned with ellipse cavities was successfully obtained. The length parallel to the elongation direction increases depending on the degree of elongation, from 6.39  $\mu\text{m}$  (diameter of cylinders) to 20.10  $\mu\text{m}$  (about 300% elongation), as shown in Figure 2b. However, the PDMS mold could only be elongated by 300% due to the limits on the



**Figure 3.** (a) Finite element analysis of the material response of the cylindrical PDMS mold to mechanical elongation. It is observed that the elongation degree of the bottom of the cavity was less than that of the top of the cavity. (b) Mechanically stretched PDMS mold held on the designed device with desirable elongation. (c) AR values are plotted for an SRM made from an entire stretched PDMS mold. (d) The area of a stretched PDMS mold that maintains uniform AR, which was used to generate SRMs with monodisperse features.



**Figure 4.** Fabrication of a diversity of shape-specific PFPE molds and particles based on the mechanical elongation process. (a) PDMS mold with cubic features replicated from a silicon master. (b) Diamond PFPE mold based on 300% first-generation elongation in the diagonal direction. (c) Longer diamond PFPE mold based on 200% second-generation elongation in diagonal direction. (d) PRINT particles replicated from mold shown in (a). (e) PRINT particles replicated from mold shown in (b). (f) PRINT particles replicated from mold shown in (c). (g) Rectangular PFPE mold based on 300% first-generation elongation along an edge of the cube. (h) Longer rectangular PFPE mold based on 200% second-generation elongation along the same edge. (i) PFPE mold based on the combination of first-generation elongation along an edge and second-generation elongation in a diagonal direction. (j) PRINT particles replicated from mold shown in (g). (k) PRINT particles replicated from mold shown in (h). (l) PRINT particles replicated from mold shown in (i). Scale bar: 20  $\mu\text{m}$ .

maximum elongation to break of the PDMS mold. In order to further extend the state of elongation, a new PDMS mold was replicated from the SRM and the same elongation cycle was repeated. As such, a second-generation PFPE mold was obtained (see Figure 2c), reaching 40  $\mu\text{m}$  parallel to the elongation direction. The elongation–replication process can be repeated for a third cycle, based on the second-generation SRM, producing yet another so-called third-generation PFPE mold possessing dramatically elongated cavities. The length of the mold in the elongation direction was over 80  $\mu\text{m}$ , nearly 13 times longer than the original template. Accordingly, once the PFPE molds are fabricated, PRINT particles can be generated through the PRINT process described above (Figure 1a). As shown in Figure 2e–h, a family of randomly distributed particles including standard cylinders and elongated worms with distinct ARs were successfully fabricated from these successive generations of stretched molds.

One major advantage of the mechanical elongation method for synthesizing patterned templates is that the AR is readily controllable by adjusting the degree of elongation. Here, the AR was determined by analysis of SEM images of particles. The length increases along the tensile axis by  $\lambda = l/l_0$ , where  $l_0$  is the initial length and  $l$  is the length after elongation. However, the elongation of the cavities in PDMS was not symmetrical when normal to the direction of stress. As the PDMS cavity is stretched, the degree of elongated deformation of the bottom of the cavity was observed to be less than that of the top of the cavity. This asymmetric elongation resulted in the formation of a “boat” shape, which resulted from the recovery tension of the connecting PDMS bulk substrate (Table 1). The elongation difference between top and bottom of the PDMS cavity that was observed, inducing the formation of such a “boat” shape, was consistent with computer simulation result, as shown in Figure 3a. The total degree of

elongation of the top of the feature was a result of the combination of every elongation step,  $\lambda = \lambda_1 \times \lambda_2 \times \lambda_3 \times \dots$ , where  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  are ascribed to the elongation degree of first, second, and third generation elongation, respectively. It is evident that the elongation of patterned features can be increased to an extreme degree with successive generations of elongation. Simultaneous with the increase in length parallel to the elongation direction, the width and height of the pattern features, normal to the elongation direction, shrink by a theoretical amount of  $\lambda^{1/2}$ .<sup>26</sup> The AR of each type of elongated particles can be well identified with analysis of length, height, and width, with AR referring to the ratio of top length,  $l_t$ , to height,  $h$ . The AR dramatically increased with the degree of elongation; an AR of 1.27 increased to 52.78 ( $>40\times$  increase) after three generations of elongation (Table 1).

To determine if the narrow size distribution of the original photolithographic master was translated throughout the elongation process, features were measured at different positions along the SRM. As shown in Figure 3c, the AR in the middle region of the stretched PDMS mold, roughly 50% of the total area, maintains feature uniformity. However, at the leading and trailing edges in the elongation direction, the AR is higher at the corners than in the middle. To ensure a uniform, monodisperse population of PRINT particles, only the center 50% region of the stretched PDMS was employed to create SRMs and subsequent PFPE molds (see Figure 3d).

The mechanical elongation method has also been extended to replication of particles with well-tuned shapes. A number of diverse shapes have been manufactured starting from a common template with islands in the shape of a cube. The cubes can display a range of deformations under stress in different directions. Rectangular and diamond shapes can be created through mechanical elongation along one edge and diagonal of the cube, respectively. First, cubes deform into diamond features when performing the elongation along a diagonal direction. As shown in Figure 4b, elongation to 300% along the diagonal resulted in the formation of diamond shapes. The diamond features can be further modified via second-generation elongation as described above. As shown in Figure 4c, after another 200% elongation, the length of the diamond shape is increased to 33.80  $\mu\text{m}$ , nearly

6 times longer than original diagonal length of the cubes, 5.80  $\mu\text{m}$ . The fabrication of particles with cubic, first- and second-generation stretched diamond shapes was accomplished by the PRINT process (Figure 4d–f). Second, in a similar fashion, cubes deform into rectangular features when performing the elongation along an edge direction. As shown in Figure 4g and h, first-generation elongation at 300% and second-generation elongation at 200% convert the cubes to a rounded rectangular shape. In comparison to molds from the original master, (Figure 4a), the feature length of the second-generation PFPE mold increased to 30.60  $\mu\text{m}$  with the width decreasing to 2.15  $\mu\text{m}$  (Figure 4h). Rectangular rods have been fabricated from these molds through the PRINT process (Figure 4j and k). Third, by applying a second-generation elongation at an angle from the first-generation elongation, more shapes are possible. Figure 4i shows the PFPE mold produced by first elongating the cubic PDMS mold by 300% along one edge followed by a 200% second elongation in a diagonal direction. This combination of elongation produces a curved parallelogram particle (Figure 4l).

## Conclusion

The mechanical elongation method presented here represents a very useful tool for the manufacture of monodisperse, asymmetric colloidal particles with a large range of aspect ratios from a single master template source. Elongated particles with aspect ratios over 40 times greater than that in the original master have been fabricated via the PRINT technique using elongated replica masters generated by mechanically deforming the molds to desired degrees in specific directions. The mechanical elongation method minimizes the need for different master templates prepared by the time-consuming and often costly photolithographic process by adapting a single master template to produce particles with a variety of shapes. It is evident that a nearly infinite library of particles with different shapes and aspect ratios could be built based on a small number of master templates. This flexibility is of vital importance for the facile fabrication of shape specific particles for applications in electronic devices, photonics, drug delivery, microfluidics, and many others.