# Electrically induced formation of uncapped, hollow polymeric microstructures

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#### **Abstract**

Uncapped, hollow polymeric microstructures were fabricated on a silicon substrate using electric field induced stretching and detachment. Initially, square or cylinder microposts were generated using a solvent-assisted capillary molding technique, and a featureless electrode mask was positioned on the top of the microstructure with spacers maintaining an air gap ( $\sim\!20~\mu\text{m}$ ). Upon exposure to an external electric field (1.0–3.0 V  $\mu\text{m}^{-1}$ ), the hollow microstructures were destabilized and stretched by the well-known electrohydrodynamic instability, resulting in contact of the top polymer surface with the mask. Subsequently, detachment of the capping layer occurred upon removal of the mask due to larger adhesion forces at the polymer/mask interface than cohesion forces of the polymer. These hollow microstructures were tested to capture the budding yeast, *Saccharomyces cerevisiae*, for shear protection.

(Some figures in this article are in colour only in the electronic version)

#### 1. Introduction

Micro-components or platforms made of polymers are currently used in biomedical devices [1], optical devices [2], microelectromechanical systems (MEMS) [3], thin-film transistors [4] and microfluidics [5] due to their unique chemical, optical and electronic properties. In general, polymers are easy to soften and chemically/physically modify, thus providing a fertile ground for various micro/nanofabrication methods ('top-down') [6] and controlled physical self-organization processes ('bottom-up') [7]. It is widely believed that a combination of these two approaches could create novel electronic or biomedical devices on micrometer length scale where the conventional lithography fails or is difficult to apply.

Recently, the self-organized structure formation of thin polymer films under the influence of an electric field has been extensively studied both experimentally [8–14] and theoretically [15–18]. In previous studies, a thin polymer layer spin coated on a solid substrate was placed between two electrodes with an air gap, and an electric field was applied

normal to the interface. Subsequently, the electric field causes an interfacial electrostatic pressure above the glass transition temperature of the polymer, driving the film into regular, self-assembled pillar arrays [8–14]. This method has the potential to provide an alternative for patterning thin polymer films with feature size less than 100 nm by using either a featureless mask or a mask patterned with protrusions of different shapes [12].

In this paper, an electric field induced self-organization method was developed to create uncapped, hollow polymeric microstructures. In this scheme, a prerequisite is to form a hollow polymeric structure prior to detachment of the capping layer. It was found that such a hollow structure could be readily formed by using a solvent-assisted capillary molding method [19–21]. This method typically consists of three steps: placing a patterned polydimethylsiloxane (PDMS) mold on the surface of a spin-coated polymer film, allowing the mold to absorb solvent and then letting the mold and the substrate remain undisturbed for a period of time until the structure solidifies after evaporation of the solvent. In particular, the geometry of PDMS mold was tailored to form a hollow structure with structure integrity instead of a simple replica that can be found

in nanoimprint or soft lithography [6]. The as-formed structure was further placed in an electric field to render an uncapped, hollow microstructure via detachment of the capping layer as described below.

## 2. Experimental methods

#### 2.1. Fabrication of silicon masters and PDMS molds

Silicon masters prepared using standard photolithography and deep reactive ion etching (RIE). First, a highly polished silicon wafer (100) was spin coated with a thick negative photoresist (KMPR-1050, MicroChem) at 500 rpm for 15 s and 1500 rpm for 30 s. The coated silicon wafer was soft baked at 65 and 95 °C for several minutes, with a brief relaxation time. The wafer was then exposed under the mask using the aligner. After developing, the wafer was placed on a hot plate at 65 and 95 °C for several minutes post-exposure baking, followed by a short relaxation time. The operating conditions of deep RIE were: 160 sccm of SF<sub>6</sub> and 16 sccm of O<sub>2</sub> (14 s active cycle, 15 W electrode power and 100 W of coil power, 21 mTorr pressure) for etching and 105 sccm of C<sub>4</sub>F<sub>8</sub> (11 s of active cycle, 80 W power, 21 mTorr pressure) for passivation. As a result of slight overetching, square or circular microposts with a smaller neck width were fabricated. For fabricating PDMS molds, a mixture of 10:1 PDMS (Sylgard 184, Dow Corning) and the curing agent was poured on the silicon master and placed at 70 °C for 1 h. The PDMS replica was then peeled from the silicon master and cut prior to use.

# 2.2. Solvent-assisted capillary molding and electric field induced detachment

To fabricate molded polymeric microstructures, silicon wafer was cleaned by ultrasonic treatment in trichloroethylene and methanol for 5 min each and dried in a mild stream of nitrogen. A few drops of the polymethyl methacrylate (PMMA) ( $M_{\rm w} =$  $1.2 \times 10^5$ ,  $T_g = 103$  °C, Aldrich) solution dissolved in toluene with various concentrations (5-30 wt%) were drop dispensed onto the silicon substrate followed by conformal contact of the PDMS mold with a slight physical loading  $(\sim 13 \text{ g cm}^{-2})$ . After solvent evaporation, the PDMS mold was removed from the wafer, resulting in well-defined molded PMMA microstructures over a large area ( $\sim 3 \times 3 \text{ cm}^2$ ). After the molding process, a featureless silicon wafer (top electrode) was placed above the pre-fabricated polymer patterns using a spacer, leaving behind a thin air gap in between ( $\sim 20 \ \mu m$ ). The spaces were  $\sim 80 \,\mu m$  thick and thus electrically isolated the substrate and the mask. The assembly was annealed above the glass transition temperature of PMMA ( $T_{\rm g} \sim 103~^{\circ}{\rm C}$ ), typically at 120 °C with application of a dc voltage (20-60 V). After annealing for a period of time (20 min to 1 h) and cooling to room temperature, the top electrode was removed from the assembly and the polymer structures were examined by a scanning electron microscope (SEM, XL30FEG, Philips Electron Co.)

#### 2.3. Cell docking inside hollow microstructures

The budding yeast *S. cerevisiae* SG3 cells were grown at 30 °C in YPD medium to an  $A_{600}$  of  $\sim$ 0.5 and the SO992 cells transformed with the plasmid  $P_{fus1}$ -GFP (S65T) were grown at 30 °C in a selective medium containing 2% dextrose to an  $A_{600}$  of  $\sim$ 0.5 (1.5  $\times$  10<sup>7</sup> cells mL<sup>-1</sup>). To capture the green fluorescent protein (GFP)-modified yeast cells onto hollow structures, a small amount of the solution ( $\sim$ 5  $\mu$ L) was dispensed onto the structure to allow for sedimentation by gravity. After cell docking, the remaining cells were washed by the medium several times and the captured cells were analyzed by using an inverted fluorescence microscope (OLYMPUS IX71, Japan).

#### 3. Results and discussion

#### 3.1. Fabrication of hollow polymeric microstructures

A schematic diagram of the experimental procedure is shown in figure 1. In the experiment, two silicon masters of an overetched pyramidal shape were used: square  $(20 \times 20 \ \mu \text{m}^2)$ at head,  $15 \times 15 \,\mu\text{m}^2$  at neck) and circular microposts (20  $\mu\text{m}$ at head, 15  $\mu$ m at neck in diameter) with the same height of  $\sim$ 60  $\mu$ m. This overetched geometry is crucial for obtaining a hollow microstructure as a result of modified capillary rise kinetics [22]. A solvent-assisted capillary molding method was used to form a hollow polymeric microstructure as shown in figure 1 [19]. This technique was originally developed as a patterning tool to reduce high pressure required for nanoimprint lithography [23]. The use of a hard, impermeable mold that is typical of imprint lithography on a solventladen film leads, however, to no pattern formation since the solvent cannot escape through the mold. It was found that a soft, permeable PDMS can provide a spontaneous, conformal contact with a solvent-laden film and forms a well-defined, three-dimensional structure by means of solvent diffusion out of the mold [19]. A major difference in our experimental scheme from previous studies is that the preformed microstructure is destabilized and further detached by the difference in adhesion forces as can be seen in figure 1. This process was made possible by the fact that the destabilized microstructure was stretched, being in contact with the mask due to the well-known electrohydrodynamic instability [15–17].

Figure 2 represents SEM images of PMMA microstructures before and after the application of an electric field. The dimensions of the silicon master were in accord with the SEM images in figures 2(a) and (b), showing good physical integrity. The thickness of spacer was  $\sim 80~\mu m$ , yielding the thickness of air gap  $\sim 20~\mu m$ . Application of an electric field then gave rise to destabilization and detachment of the pre-fabricated pyramidal structures, resulting in uncapped, hollow microstructures as shown in figures 2(c) and (d). The presence of empty inner spaces was verified by the cross-sectional SEM images in figures 2(e) and (f), indicating that the solution wet the corner but did not fill the entire spaces of the cavity.

The entire process consists of three sequential steps: molding, stretching and detachment. A possible mechanism for the formation of a hollow structure is that the solution

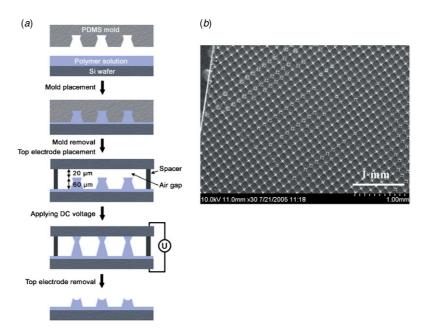


Figure 1. (a) A schematic diagram of the experimental procedure. First, square or cylinder microposts were generated using a solvent-assisted capillary molding technique and a featureless electrode mask was positioned on the top of the microstructure with spacers maintaining an air gap ( $\sim$ 20  $\mu$ m). Upon exposure to an external electric field (1.0–3.0 V  $\mu$ m<sup>-1</sup>) followed by removal of the top electrode, the hollow microstructures were stretched by the well-known electrohydrodynamic instability, resulting in detachment of the capping layer. (b) One example of large area fabrication with slight structural heterogeneity is shown. The experiment was reproducible (>70%) and could be applied to a broad range of surface areas from 2 × 2 mm<sup>2</sup> to 3 × 3 cm<sup>2</sup>.

first wets the corner of the mold and starts to rise on the slanted wall having an acute angle [24]. At this time, the meniscus is localized such that the film around the periphery of the mold progresses without merging. This capillary rise is counterbalanced by gravitational force and thus a slanted wall facilitates the capillary movement in comparison to a vertical wall. After the solution reaches the neck position, it further fills the pyramidal head with a curvature change, completing the capillary rise with empty inner spaces.

The stretching of the molded microstructure can be explained by the well-known electrohydrodynamic instability. The driving force of this instability is the electrostatic force, which increases with increasing film thickness (or increasing charge density at the polymer/air interface) and with decreasing width of the air gap [11]. In our approach, the thickness of the air gap is smallest at the top of the protruding microstructure, allowing for the largest electrohydrodynamic forces. Furthermore, the stretching was much facilitated by increasing the temperature above  $T_{\rm g}$ , rendering high polymer and charge mobility compared to room-temperature process [10]. The stretching resulted in physical contact of the capping layer with the top electrode and then the detachment occurred upon removal of the mold at the neck position.

# 3.2. Theoretical explanation for the formation of hollow microstructures

To gain an understanding of the physics involved in the electrically induced stretching and detachment of structured polymer surface, we first consider the competition between the electrostatic driving force and the yield stress of the patterned polymer during the elongation. The electrostatic force that is

generated between two parallel plates is given by [25]

$$F = \frac{\varepsilon_0 S U^2}{2I^2} \tag{1}$$

where  $\varepsilon_0$  is the permittivity of free space, S is the surface area of a plate, U is the applied voltage and l is the air gap space. When we insert U=45 V,  $S=20^2$   $\mu\text{m}^2$ ,  $\varepsilon_0=8.85\times 10^{-12}$  F m<sup>-1</sup> and l=20  $\mu\text{m}$ , the resulting electrostatic force is  $8.97\times 10^{-9}$  N or 22.4 Pa. For elongation, the magnitude of the electrostatic force needs to be larger than the yield stress of the polymer. Typically, the yield stress of PMMA ranges from 52 to 71 MPa at room temperature [26], which monotonically decreases with increasing temperature. In particular, this value drops drastically at the glass transition and might be negligible at the temperature ( $\sim 120$  °C) used in this study [27]. Thus, the PMMA microstructure could be readily stretched above  $T_g$ , which is also supported by the experimental observation that the stretching was nearly suppressed at room temperature.

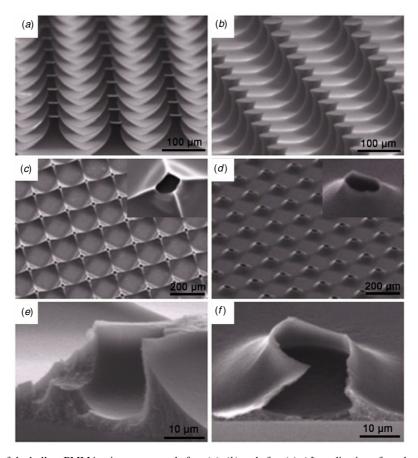
Second, we consider the competition between the adhesion force at the top electrode and the cohesion force of PMMA. The operability of the detachment can be given by [28]

$$W_{\rm a} > W_{\rm c}$$
 (2)

with  $W_a$  being the work of adhesion at the PMMA/silicon interface and  $W_c$  being the work of cohesion of PMMA. The work of adhesion can be calculated by the harmonic mean method, yielding [29]

$$W_{\rm a} = 4 \left( \frac{\gamma_1^{\rm d} \gamma_2^{\rm d}}{\gamma_1^{\rm d} + \gamma_2^{\rm d}} + \frac{\gamma_1^{\rm p} \gamma_2^{\rm p}}{\gamma_1^{\rm p} + \gamma_2^{\rm p}} \right)$$
(3)

where the superscripts d and p are for the dispersion and polar component of the surface tension  $\gamma$ , respectively. With



**Figure 2.** SEM images of the hollow PMMA microstructures before (a), (b) and after (c), (d) application of an electric field of 2.5 V  $\mu$ m<sup>-1</sup>. Two pyramidal dimensions were used: (a), (c), (e) square head and neck of 20 × 20 and 15 × 15  $\mu$ m<sup>2</sup>, respectively, and (b), (d), (e) circular head and neck of 20 and 15  $\mu$ m in diameter, respectively. The inset images in (c), (d) show a magnified view. The presence of cavity was verified by cross-sectional SEM images in (e), (f).

**Table 1.** Measurements of contact angles of water, diiodomethane on PMMA and silicon substrate and the resulting surface tension values using the harmonic mean method.

	Contact angle (°)		Surface tension (mJ m <sup>-2</sup> )		
	Water	Diiodomethane	$\gamma^{\mathrm{d}}$	$\gamma^{\mathrm{p}}$	$\gamma = \gamma^{d} + \gamma^{p}$
PMMA Silicon wafer	60.6 31.0	64.6 45.0		23.9 39.6	

probe liquids of water and diiodomethane, the contact angles on PMMA and silicon surfaces were measured, which in turn provided the surface tension values that are needed to calculate the work of adhesion in equation (3). The results are summarized in table 1, showing that the calculated work of adhesion was 99.1 mJ m<sup>-2</sup>. In parallel, the work of cohesion can be roughly estimated by twice the surface tension of PMMA [29]:

$$W_{\rm c} = 2 \cdot \gamma_1 \tag{4}$$

where  $\gamma_1$  is the surface tension of PMMA. The calculated work of cohesion was 82.2 mJ m<sup>-2</sup>, which supports the validity of the detachment process shown in equation (2).

To examine the effects of the magnitude of electric field on the structure formation, the electric field was varied from 1.0 to 3.0 (V  $\mu m^{-1}$ ) while maintaining the other conditions the

same. As shown in figure 3(a), the stretched length appears to increase linearly with the electric field. Furthermore, a critical electric field seems to exist ( $\sim$ 2.0 V  $\mu$ m<sup>-1</sup>), above which the detachment process took place after elongation of the polymer. The presence of a critical electric field suggests that the detachment should be aided by physical contact of the polymer surface with the top electrode. Shown in figure 3(b) is the stretched polymer structure without detachment that was obtained at an electric field of  $1.5 \text{ V } \mu\text{m}^{-1}$ . It can be seen from the figure that the pyramidal head was elongated with slight reduction in neck width. As the process was conducted at 120 °C, most of the pyramidal heads were collapsed after removal of the top electrode.

# 3.3. Cell docking inside hollow microstructures

To seek potential applications of the hollow microstructures presented here, the budding yeast, *S. cerevisiae*, was used to test cell docking. It is hoped that aforementioned microstructures could protect the captured cells from shear flow in various biological applications owing to their unique shape. *S. cerevisiae* is now recognized as a model system representing simple eukaryotic organisms whose genome can be easily traced and manipulated [30]. Some of the

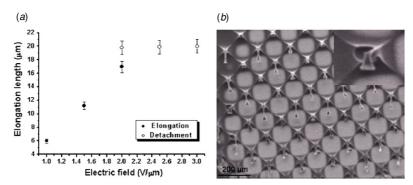


Figure 3. (a) Effects of the magnitude of electric field on the structure formation. For detachment, an electric field larger than  $\sim$ 2.0 V  $\mu$ m<sup>-1</sup> needed to be applied. (b) An example of the stretched polymer structure without detachment that was obtained at an electric field of 1.5 V  $\mu$ m<sup>-1</sup>. The inset shows an enlarged view.

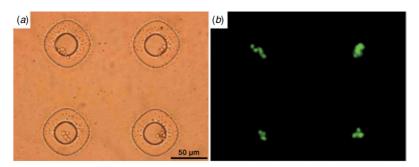


Figure 4. (a) Brightfield and (b) fluorescent images of the captured SG3 yeast cells (autofluorescent) inside circular microwells (30  $\mu$ m in diameter).

properties that make yeast particularly suitable for biological studies include rapid growth, high dispersion, easy genetic manipulation and mutant isolation. Therefore, it would be of benefit for biological research to develop a simple method to capture cells in a shear-protecting manner [31, 32].

Figure 4 shows (a) brightfield and (b) fluorescent images of the captured SG3 yeast cells (autofluorescent) inside circular microwells (30  $\mu$ m in diameter). It can be seen from the figure that three to six cells were docked inside the microwells with strong expression of GFP, indicating that the cells are viable and could be used for further biological or biochemical studies. In addition to docking of the yeast cell, the current method could also be used to capture mammalian cells, small biological species or inorganic particles. To do this, one needs to have precise control over various parameters such as geometry of mold, surface tension, viscosity and film thickness of polymer since the formation of the hollow structure strongly depends on these parameters. Although 20  $\mu$ m circular and square microposts have been used in this study, it seems that smaller or larger structures could also be fabricated with appropriate scale down or scale up of mold geometry and film thickness. For capturing individual nanoparticles or small biological species including DNA and virus, the neck opening should be less than  $\sim 100$  nm but the preparation of a mold with slanted wall would be challenging. For capturing mammalian cells, the neck opening should be larger than  $\sim 20 \ \mu m$  for ensuring a reasonable height for docking. This necessitates a relatively large film thickness that is not easily prepared from spin-coating or drop-casting.

#### 4. Summary

We have presented the electrically induced formation of uncapped, hollow polymeric microstructures. The entire process consists of solvent-assisted molding, electric field induced stretching (i.e., the electrohydrodynamic instability) and detachment of the capping layer mediated by larger adhesion forces at the polymer/electrode interface. It was found that a relatively high electric field was needed to ensure the detachment process along with the stretching of polymer structure. The hollow microstructures were further tested to capture the budding yeast cell in a shear-protecting manner. Our method can be applied to creating unique microreactors or cell-based microfluidic platforms that are not easily accessible by conventional lithographic techniques.

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