Rolling particle lithography by soft polymer microparticles

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SUPPLEMENTARY INFORMATION

1. Master fabrication and particle realization

For the fabrication of the master *A* (*B*), a layer of SU-8 2025 (2100) is deposited onto Si by spin-coating at 500 rpm for 5 s (10 s) followed by 1750 rpm (3000 rpm) for 30 s. The resist undergoes a thermal treatment (prebake) at 65 °C for 2-5 min and at 95 °C for 7-25 min to guarantee the complete evaporation of the solvent. Then the resist is exposed to UV light for 20 s and thermally cured (post-exposure bake) at 65 °C for 1 min and 95 °C for 5-15 min. The pattern is developed and rinsed by isopropanol. A final hard-bake is carried out at 150 °C for 7-10 min.

The used PDMS microfluidic devices are fabricated by standard soft lithography and SU-8 photolithography methods and used to generate emulsions (Fig. 1). Briefly, two immiscible fluids are simultaneously injected into the microfluidic system, with the dispersed phase (liquid PDMS) supplied from the central inlet channel and the continuous phase (water and surfactant) supplied from the two side channels. Regular emulsion droplets are clearly imaged in an observation chamber (1 cm in width, downstream of the cross channel), which slows down the flow (Fig. 1c). The particles size is easily tailored by the flow-rate of the continuous phase in the range 10-110 μL min^{-1}, in a device with channel height of 80 μm (Device *B*). For instance, Fig. 1f displays microparticles generated by flow rates, Q_c = 55 μL min^{-1} and Q_d = 1 μL min^{-1}, which results in a Gaussian distribution peaked at 162 μm with a dispersity index [(standard deviation/average diameter)×100] of about 5% (Fig. 1g). We also observe that for dispersed phases flowing with Q_d > 1.0 μL min^{-1}, a co-laminar flow forms without generating droplets.[S1]

2. Characterization

The size distribution for solid microparticles is determined analysing various micrograph images with resolution of 3872×2592 pixel, and studied using freeware scanning probe microscopy software (http://gwyddion.net/). Scanning electron micrographs are collected with an acceleration voltage of 2 kV and an aperture size of 30 μm, with particles lying on a Si substrate and depositing a conductive pre-coating (an Au layer of thickness 5-10 nm).

The emission of patterns is characterized by an inverted fluorescence microscope equipped with a high-pressure Hg lamp (HBO100, Zeiss), wide-excitation blue and green filter sets and a coupled colour CCD camera (8 Megapixel, model DFC490, Leica). All the optical characterization is carried out at room temperature under air atmosphere soon after printing to avoid degradation effects of the dyes.

3. Modelling

Frictionless contact constraints are enforced at the interface between the bodies, and due to the symmetry of our geometry, it is possible to analyze only one eight of the system upon application of the appropriate boundary conditions on the symmetry planes. The non-penetration constraint is enforced with the penalty method, using a conveniently large penalty parameter so as to obtain minimal penetration errors while avoiding ill-conditioning of the global stiffness matrix. The hyperelastic neo-Hooke material law contains two unknown parameters, namely the elastic modulus (E_2) and the Poisson's coefficient (v_2). Assuming nearly incompressible material behavior, the latter is set to 0.49, leaving E_2 as the only unknown to be calibrated from test results. The value of E_2 is calibrated from an experimental applied-load vs. top displacement curve by minimizing the root mean square deviation (*RMSD*) between experimental and numerical results, defined as:

$$RMSD = \sqrt{\sum_{i=1}^{n} (F_{exp,i} - F_{num,i})^2 / n}$$

where $F_{exp,i}$ and $F_{num,i}$ are the i^{th} experimental and numerical values of the load, and n is the number of points used in the calibration. Comparison with an independent contact diameter vs. top displacement curve is finally used for independent verification.

4. RPL Lithography

Employing particles with high size uniformity is crucial for achieving good pattern transfer by RPL, and fabrication of elastomeric microspheres by multi-phase microfluidics is strategic in this respect. Polydispersion indexes above 10% would not guarantee a uniform applied pressure on different particles, which in turn would prevent the control of the final resolution. Once particles that are highly uniform in size are obtained, the pattern transfer accuracy of RPL is limited only by the mechanics of the system used for controlling the motion and vertically compressing the microspheres. In addition, we observe that a good

control of the translational speed of the slides or stages, that in turn impart the rolling motion to inked particle, is needed for obtaining sharp edges of the patterned features. In fact, rough edges of printed features correspond to locally reduced speeds of the RPL particle, which determine an excess of delivered inks and ultimately a local loss of resolution.

After inking RPL particles, determining the exact position where start writing implies a controlled delivery of the particle onto the target substrate. For particles with size down to tens of μm, this can be performed by mechanical methods through manual or motorized stages with μm-accuracy and registration capability (in case of needed overlay alignment or accurate delivery on pre-defined patterns on the target substrate). This is possible because the particles naturally adhere to flexible glass substrates (24×60 mm^2, thickness 130-160 μm, Bio-Optica) upon slight compression. A subsequent, slight mechanical bending of the glass slide allows to deliver the particles onto the final surface to be patterned. Overlay alignment is easily accomplished by means of X-Y-Z conventional optical mounting or mask aligners for multilevel soft lithography.[S2] Once the particle is delivered, the upper pressing glass slide is mounted on a micrometer stage by screw clip connectors, and carefully approached to the elastomeric sphere, with typical approaching speed of 10 μm s^{-1}. Pre-defined patterns (Fig. 3a-f, Fig. S1) or alignement markers on the target substrate helps in positioning the particle and in controlling its motion in real-time during lithography. We anticipate that for smaller particles other highly controlled, non-mechanical methods can be useful for particle approach, such as optical tweezers [S3] or by dynamic magnetic control enabled by doping the elastomeric sphere by magnetic nanoparticles. After the lithographic process the elastomeric sphere is removed from the substrate by using a glass slide with sticky coating (realized by *in situ* polymerization of PDMS with a mixture of base and curing agent in the ratio 20:1) compressed against the PDMS sphere. No effect is appreciable on the microcontact from either the solution concentration in the used ranges, or the various tested substrate material (glass, silica and Gold).

Multiple particles are rolled simultaneously with high control along arbitrarily complex patterns by means of a 3D multi-axes piezostage (P-562.3CD, Physik Instrument), mounted on an inverted microscope (Axiovert 40, Zeiss) (Fig. S2, Fig. S3).

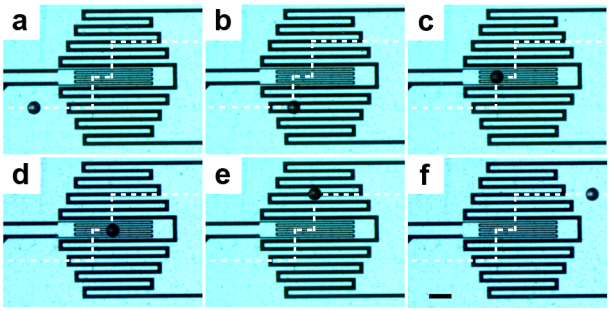

Fig. S1. Optical micrographs of a particle at various time instants, rolling on a pattern made of metal electrodes. Marker = 300 μm.

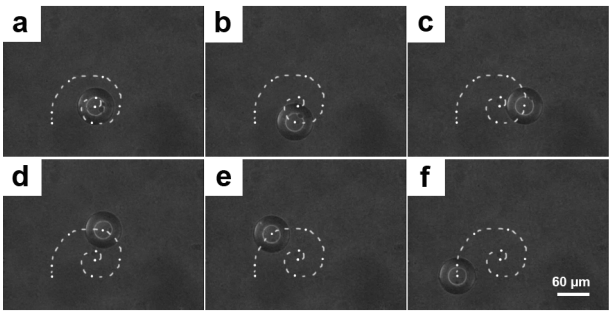

Fig. S2. Optical micrographs of a particle at various time instants, while being controlled along a spiral pattern by a piezo-stage. From a to f, time = 3 s, 33 s, 48 s, 63 s, 78 s, and 98 s. Microsphere average velocity ≅ 10 μm s^{-1}.

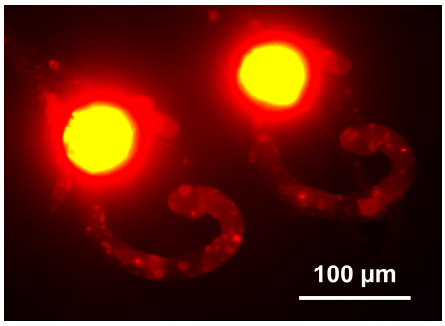

Fig. S3. Fluorescent micrographs of two particles rolling along spiral patterns. Both the highly fluorescent particles and the delivered light-emitting patterns are visible in the figure.

S1 S. L. Anna, N. Bontoux and H. A. Stone, *Appl. Phys. Lett.* 2003, **82**, 364.

S2 S. Pagliara, L. Persano, A. Camposeo, R. Cingolani and D. Pisignano, *Nanotechnology* 2007, **18**, 175302.

S3 R. Omori, T. Kobayashi and A. Suzuki, *Opt. Lett*. 1997, **22**, 816.