

[Supporting Information]

Array of nanoscale lenses for subwavelength optical lithography

Jae-Won Jang,^{1,2,4†} Zijian Zheng,^{1,2,5,†} One-Sun Lee,^{1,2†} Wooyoung Shim,^{2,3} Gengfeng Zheng,^{1,2} George C. Schatz,^{1,2,*} and Chad A. Mirkin^{1,2,3,*}

¹Department of Chemistry, Northwestern University,

²International Institute for Nanotechnology, Northwestern University

³Department of Materials Science and Engineering, Northwestern University

2145 Sheridan Road, Evanston, IL 60208-3113.

*Corresponding authors

Chad A. Mirkin

Electronic mail: chadnano@northwestern.edu

Phone: (847) 467-7302

George C. Schatz

Electronic mail: schatz@chem.northwestern.edu

Phone: (847) 491-5657

[†]Equal contributions.

⁴Current address: NanoInk, Inc., 8025 Lamon Avenue, Skokie, IL 60077

⁵Current address: Institute of Textiles and Clothing, the Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR.

Experimental Section

PEG lens fabrication: PEG polymer nano and micro scale lenses were fabricated by DPN-patterning experiments, which were carried out with an NSCRIPTOR™ (NanoInk, Inc., Skokie, IL) and commercially available 1 dimensional (1D) pen arrays (Si₃N₄, Type M, NanoInk, Inc.). 1D pen arrays were coated with PEG (MW 2,000, 35,000, and 10,000 Daltons, Sigma–Aldrich) by tip dipping in 5mg/mL PEG acetonitrile solution for 30 s. All DPN-patterning experiments were carried out under controlled humidity and temperature (93% or 30% relative humidity, 28 °C). HMDS material was spin-coated on quartz substrates with 5000 rpm for 20 s. The HMDS coated quartz substrates were baked at 100 °C for 1 min, prior to DPN deposition of PEG.

UV lithography: photolithography experiments were carried out with a mask aligner (Q-4000, Quintel) and positive-type photoresist (S1805, MicroChem Inc.). Normal UV line ($\lambda = 365$ nm) was irradiated by different exposure times. Developing was carried out by commercially available developer (MF319, MicroChem Inc.) for 1 min.

Finite element modeling: FEM simulations were performed using Comsol (Comsol, Inc). Modeling was performed for cases with the photomask in free space to calculate the focal length of PEG lens, and in contact with a layer of photoresist to calculate the intensity of light with the transverse electric mode (The model is shown in the inset of Figure 3a). The wavelength of the incident light was 365 nm, and the periodic boundary conditions at the lateral edges of the system were used. The values of the refractive index of the materials used are $n_{\text{HMDS}} = 1.407$, $n_{\text{silicon}} = 6.54 - 2.89i$, $n_{\text{air}} = 1.0$, $n_{\text{PEG}} = 1.43$, and $n_{\text{photoresist}} = 1.71 - 0.04i$.¹

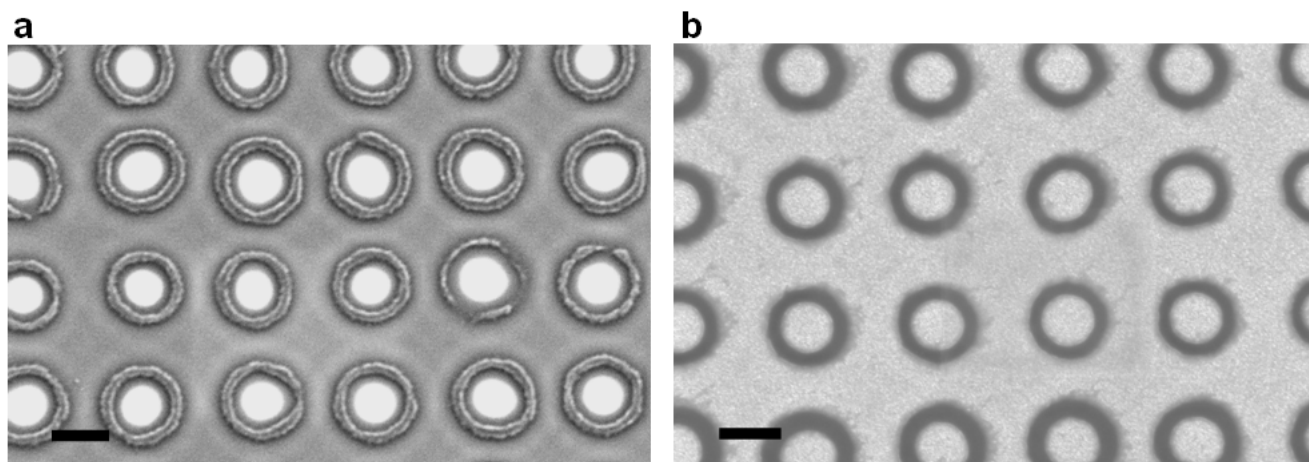


Figure S1. SEM images of typical (a) well- and (b) ring-shaped positive photoresist (S1805) features fabricated by PEG (MW 2,000) lens phase-shift photomask. Each photoresist features were fabricated by (a) 4 s and (b) 6 s UV exposure times, respectively. The critical resist development time (t_c in **Figure 1**) is approximately 5 s in the case of the PEG (MW 2,000) lens phase-shift photomask. Scale bars are 2 μm .

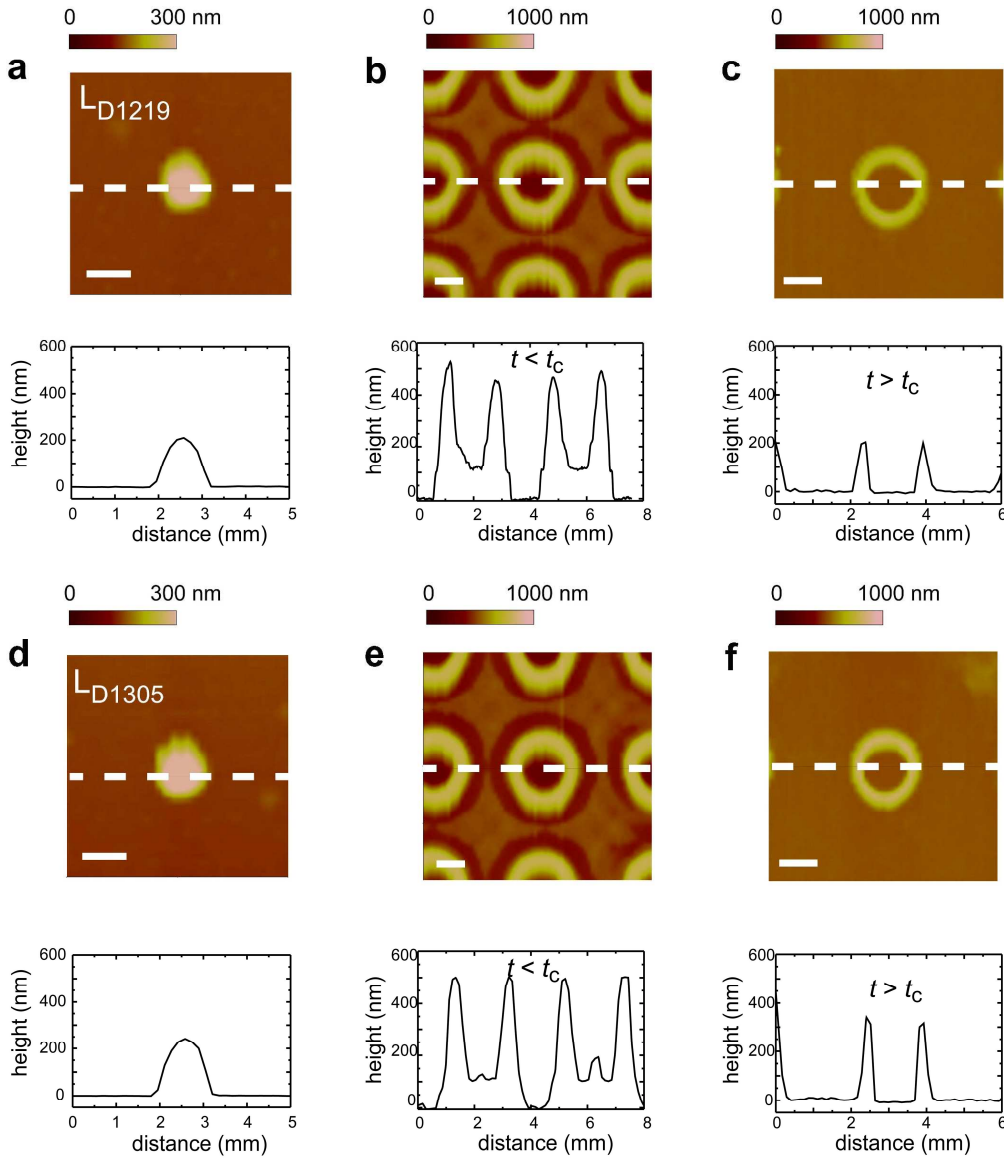


Figure S2. (a) Tapping mode AFM topographic image and cross sectional line profiles of a PEG lens (MW = 100,000) with a diameter of 1219 nm. The dwell time of the tip was 5 s. (b) The cross sectional profile of a positive photoresist feature generated from the PEG lenses in **a** with a UV exposure time of 3 s. (c) The positive photoresist feature generated when UV exposure time was 5 s. (d) Tapping mode AFM topographic image and cross sectional line profile of a PEG lens with a diameter of 1305 nm (dwell time was 10 s). (e) The cross-sectional line profile of a positive photoresist feature generated by a PEG lens in **d** with a UV exposure time of 3 s. (f) A similar feature, but after a UV exposure time of 5 s. The path for the AFM cross section line profiles are denoted by the white dashed lines. The length of the scale bar in each figure is 1 μm .

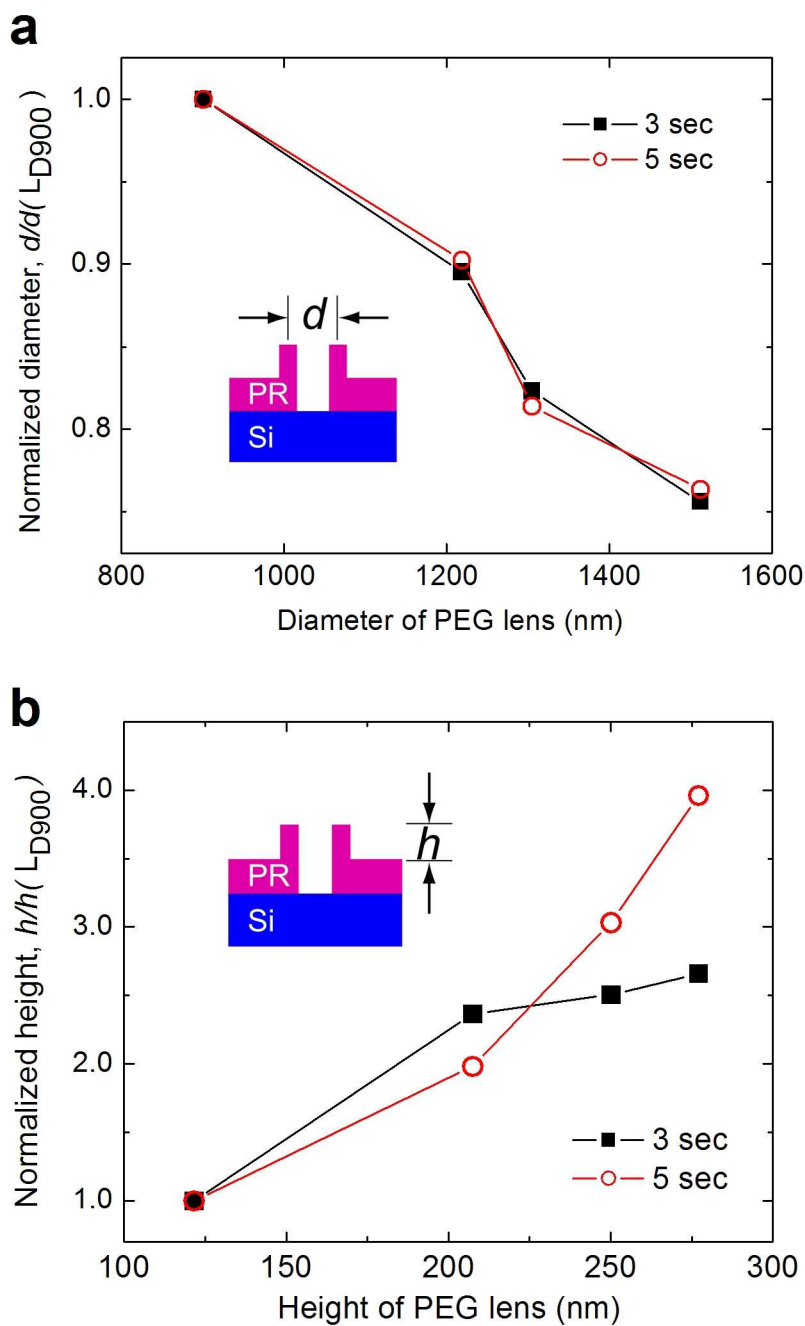


Figure S3. (a) A plot of normalized diameter of photoresist features vs. the diameter of PEG lens at UV exposure time of 3 and 5 s. (b) A plot of normalized height of photoresist features. The normalization is executed by dividing by the photoresist data values fabricated by L_{D900} . The data of PEG lens are from L_{D900} , L_{D1218} , L_{D1305} , and L_{D1512} in **Figures 2** and **S2**, in the order of increase of lens dimension.

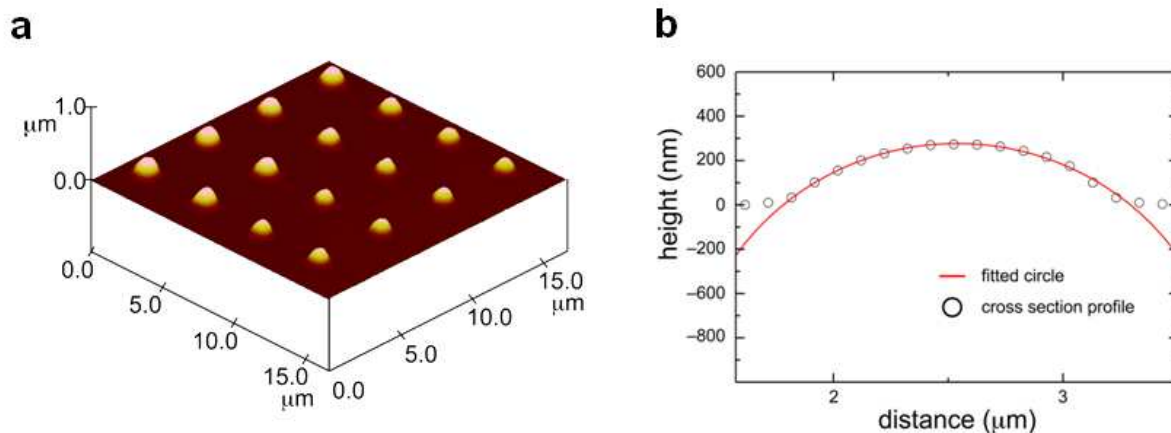


Figure S4. (a) 3-dimensional tapping mode AFM topographic image of PEG lens array. Left two rows of the bigger PEG lens was fabricated by a tip dwell time of 10 s, and the other smaller PEG lenses was fabricated by 5 s dwell time. Molecular weight of PEG was 35,000 Daltons. (b) The plot of tapping mode AFM cross sectional profile of PEG lens fitting by perfect circle. AFM profile of PEG lens shows the near spherical shape.

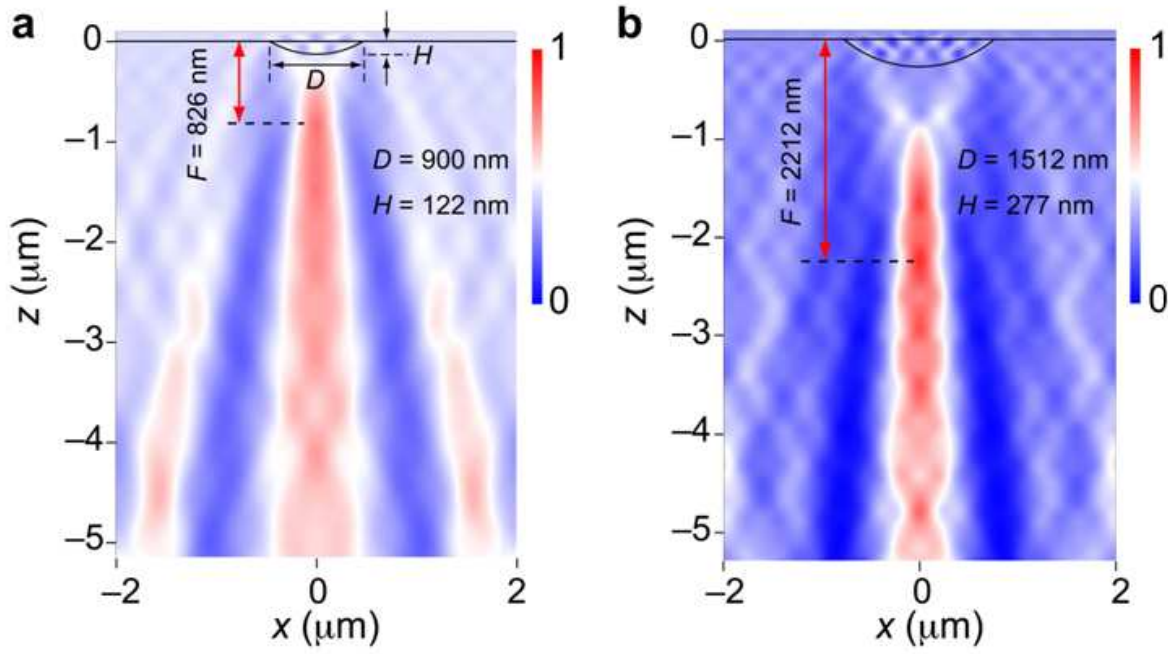


Figure S5. FEM simulation of the focal length of the PEG lens. A photomask in free space is used in the simulation. The focal length for L_{D900} and L_{D1512} is (a) 826 nm and (b) 2212 nm. The focal length is determined by the distance from the lens bottom to the maximum light intensity position along $x = 0$. The focal length is 826 nm for L_{D900} , and it is 2212 nm for L_{D1512} . The focal length from the simulation is shorter than the focal length calculated from the geometric optics equation, $F = R/(n - 1)$, where F is focal length, R is the radius of PEG lens and n is the refractive index of PEG, 1.43. This geometric optics focal length is 2080 nm (L_{D900}) and 2722 nm (L_{D1512}), so the focal length from the simulation is ~40 % relative to the value calculated from the geometric optics equation for L_{D900} and ~81 % for L_{D1512} . The shorter focal length of the FEM simulation compared to geometrical optics is consistent with a previous report.²

Reference

1. Maria, J.; Malyarchuk, V.; White, J.; Rogers, J. A. *J. Vac. Sci. Technol. B* **2006**, 24, 828-835.
2. Lee, J. Y.; Hong, B. H.; Kim, W. Y.; Min, S. K.; Kim, Y.; Jouravlev, M. V.; Bose, R.; Kim, K. S.; Hwang, I.-C.; Kaufman, L. J.; Wong, C. W.; Kim, P.; Kim, K. S. *Nature* **2009**, 460, 498-501.