Electronic Supplementary Information for:

Confinement templates for hierarchical nanoparticle alignment prepared by azobenzene-based surface relief gratings

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S1: Schematic top view of the illuminated area

The holographic inscription process was carried out to generate SRGs with a spot diameter of 1 to 2 mm. While the grating periodicity (schematically indicated by vertical lines in Figure S1) remains constant over the whole spot size (cf. S2), the grating height decreases from the center to the edges due to Gaussian beam profile (cf. S3). An area with an approximately constant grating height exists around the center (blue circle) of the spot. For comparison, the typical size of an AFM image is shown in red.

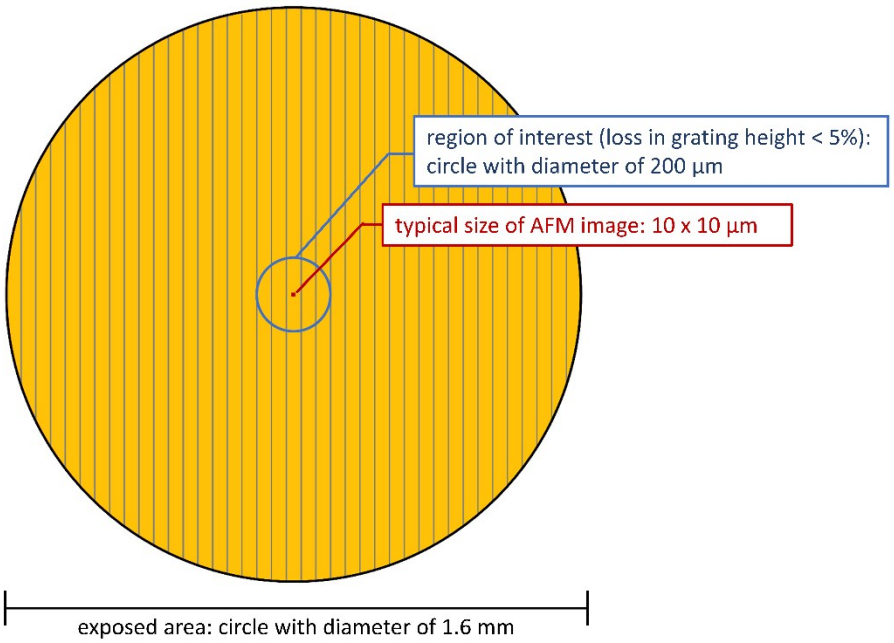

Figure S1: Scheme of the inscribed SRG spot with the indicated region of interest. The experiments were analyzed within this region.

S2: Variation of grating period within the exposed area

We analyzed the variation of grating period and grating height along the entire exposed area of a PDMS replicated SRG. Over the entire area, the grating period remained constant. Treatment with oxygen plasma had no influence on this parameter.

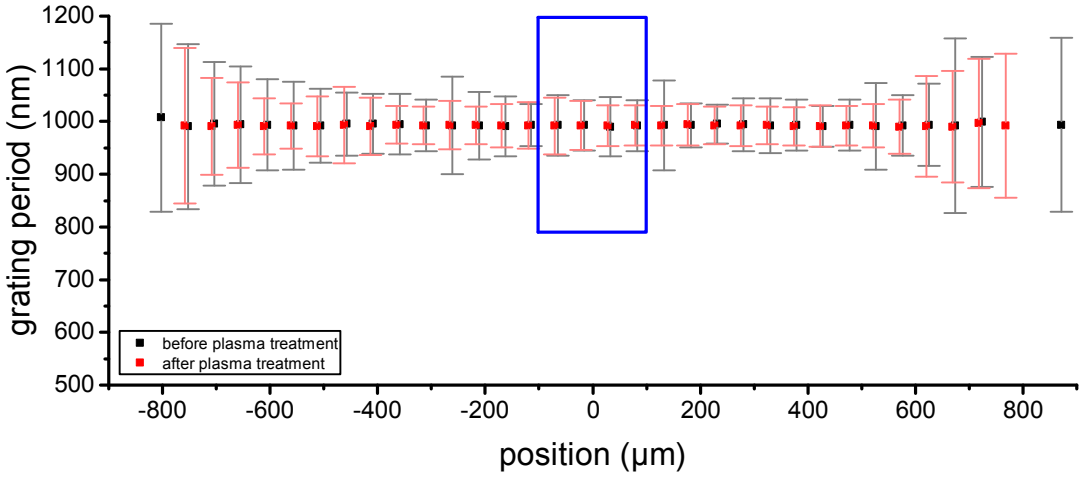

Figure S2: Variation of the grating period across the diameter of the exposed area of a PDMS replicated SRG before and after plasma treatment. The blue frame indicates the central region of interest for experiments.

S3: Variation of grating height within the exposed area

The grating height has a maximum in the center of the PDMS SRG spot and decreases to the outside. It follows a Gaussian curve which can be attributed to the Gaussian beam intensity profile of the laser used to inscribe the gratings onto the azo film. Within a radius of about 100 µm around the central maximum, the grating height decreases by less than 5%. During surface activation by plasma etching, the overall grating height decreases by about 20%.

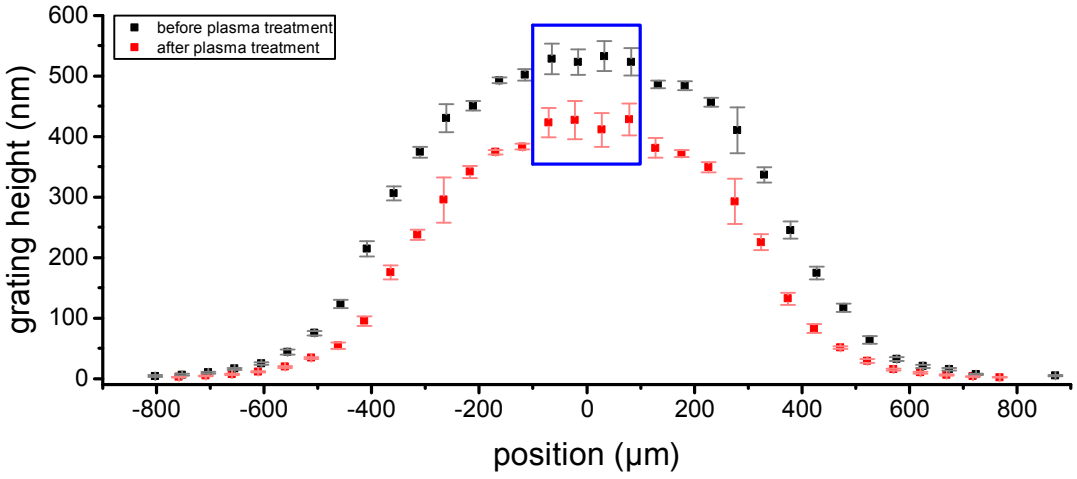

Figure S3: Variation of the grating height across the diameter of the exposed area of a PDMS replicated SRG before and after plasma treatment. The blue frame indicates the central region of interest in which the decrease of grating height is less than 5%.

S4: Comparison of holographic writing and strain-release wrinkling

Due to the optical inscription process, surface relief gratings are defect-free over large areas. To demonstrate this, large-area AFM height images of 90 x 90 µm were recorded. Figure S4A depicts a typical AFM height image of a PDMS SRG which was recorded in the central region of the exposed area. No defect structures are observable. In contrast, corrugated surfaces of similar dimensions fabricated via strain-release wrinkling show several defects (Figure S4B). In the stiff plasma-oxidized surface layer on a uni-axially pre-strained, compliant PDMS substrate, not only parallel periodic surface wrinkles formed upon release of the strain which are oriented perpendicular to the strain direction.[1–3] Due to lateral expansion, the brittle layer can form irregular cracks parallel to the stretching direction. Moreover, so-called y-branches can develop, if several regions of wrinkles merge together.[4]

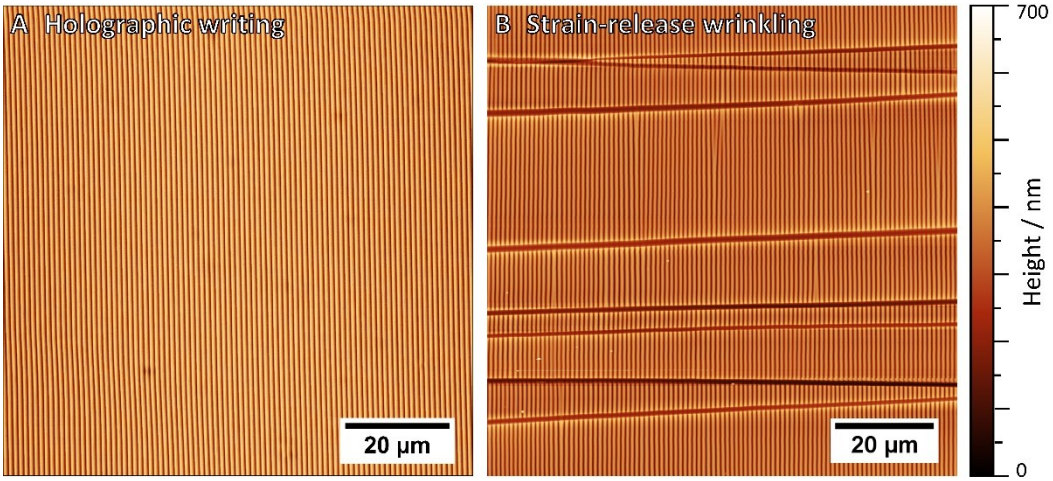

Figure S4: AFM height images of corrugated surfaces. Surface relief grating replicated with PDMS (A). Grating period is 1.0 µm, grating height 580 nm. No significant defect structures are observable over large areas. Parallel surface wrinkles, grating period 892 ± 67 nm and grating height 261 ± 22 nm, showing cracks and y-branches as defects (B).

References:

(1) Bowden, N., Brittain, S., Evans, A. G., Hutchinson, J. W., Whitesides, G. M. Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer. *Nature* **1998**, *393*, 146–149.

(2) Schweikart, A., Fortini, A., Wittemann, A., Schmidt, M., Fery, A. Nanoparticle assembly by confinement in wrinkles: Experiment and simulations. *Soft Matter* **2010**, *6*, 5860.

(3) Efimenko, K., Rackaitis, M., Manias, E., Vaziri, A., Mahadevan, L., Genzer, J. Nested self-similar wrinkling patterns in skins. *Nat. Mater.* **2005**, *4*, 293–297.

(4) Li, Z., Zhang, S., Zhang, P., Yang, D., Jin, G., Ma, H. Surface initiated polymerization from integrated poly(dimethylsiloxane) enables crack-free large area wrinkle formation. *Polym. Adv. Technol.* **2012**, *23*, 1240–1245.

S5: Layout of the SRG substrate for particle alignment

We aligned the polystyrene nanoparticles on replicated PDMS SRGs via spin coating. To this end, we prepared a circular master sample with a diameter of 5 cm and inscribed 8 SRG spots with inscription times between 5 and 70 s (Figure S5). The SRGs are oriented towards the center.

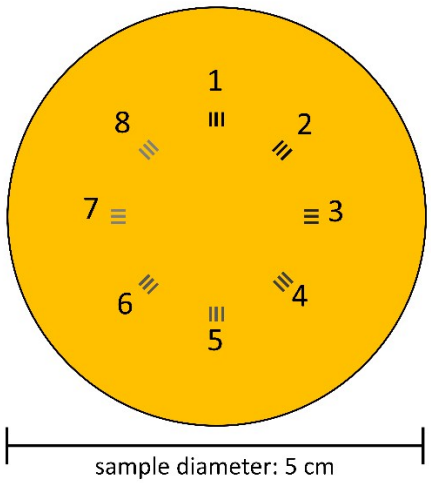

Figure S5: Circular master sample with 8 inscribed SRG spots for particle alignment via spin-coating.

S6: Dimensions of particles used for the alignment investigations

Particle dimensions were measured via AFM analysis of dried PS latex particles on a silicon wafer. The evaluation of 136 individual particles reveals a mean diameter of 186 ± 4 nm (Figure S6).

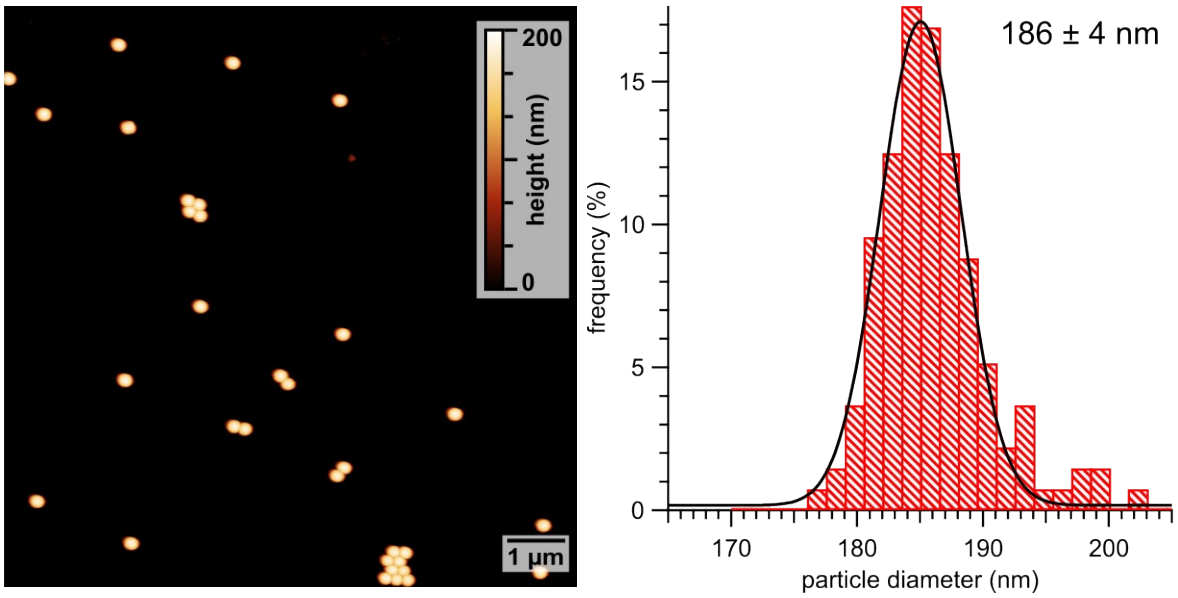

Figure S6: AFM analysis of particle dimensions. Representative AFM height image of PS latex particles dried on a silicon wafer (A). Diameter histogram of 136 particles evaluated (B).