Shape Control of Multivalent 3D Colloidal Particles via Interference Lithography

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Laser setup: 2D and 3D patterns were fabricated using multi-beam holographic interference lithography that allows generation of periodic structures over large areas with high resolution. The fabrication involved the sequential, double exposure to the interference pattern of two equal intensity laser beams for the 2D square lattice and single exposure to the interference pattern of six equal intensity laser beams for simple cubic 3D structure and the transfer of the resultant intensity pattern into an SU8 photoresist platform via laser-initiated cationic polymerization. The Gaussian output from the laser was cleaned up and expanded using a spatial filter and re-collimation setup: the beam was expanded by a factor of ~2 for the 2D square lattice; a set of bi-convex lenses with focal lengths of 80mm and 171mm were used to expand the beam by a factor of ~2 for the 3D simple cubic structure. The light intensity distribution depends on the relative directions and polarizations of the interfering beams. For the case of the 2D square structure, a 2-step sequential exposure with a 90° rotation of the sample on a rotation stage between exposures was used where orthogonal sets of gratings were exposed onto the resist. A light coupling prism was not utilized for the fabrication and corrections in the k-vectors and beam polarizations were accounted for in the

modeling of the level sets of the interference patterns. For the 3D simple cubic structure, prisms with an index equal to that of the photoresist with faces perpendicular to the incoming beams were employed to prevent refraction of the incident beams. The beam geometry and the prism configuration used are shown in Figure S1.
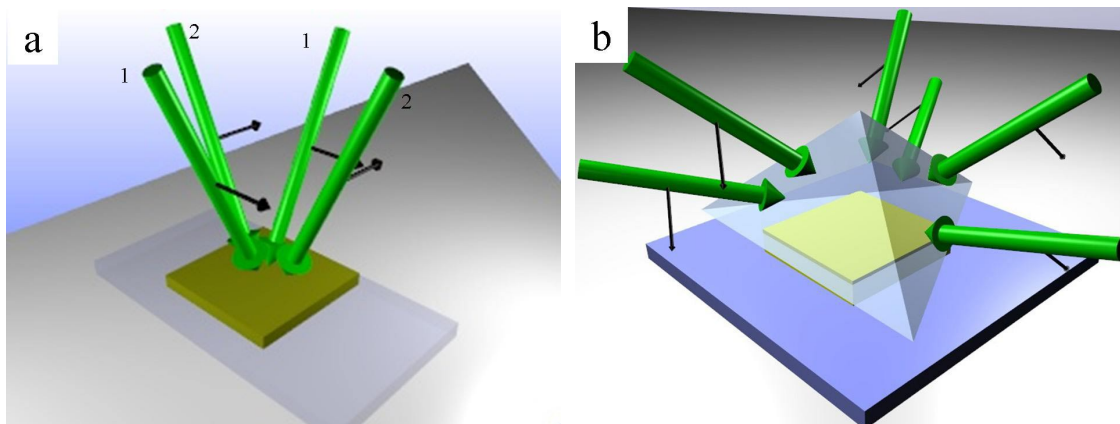

Figure S1. Schematic illustration showing the beam geometry and the prism configuration for double exposure of the 2D square structure (a) and for the single exposure of the 3D simple cubic structure.

Preparation of 2D and 3D bicontinuous structure: The materials platform consisted of Epon-SU8 (Shell) as a photoresist (a multifunctional epoxy derivative of a bisphenol-A Novolac), H-Nu 470 (Spectra group) as a photosensitizer which absorbs the visible light and electron transfers to an onium salt, octoxyphenylphenyliodonium hexafluoroantimonate (OPPI) (UCB Radcure) as a photoacid generator, and trioctylamine to compensate the non-zero background arising from the interference intensity. The glass support was treated with a thin (700 nm) buffer layer of pre-crosslinked SU8 material to assure firm attachment of the structured polymer film to the substrate via chemical grafting. An 8 µm thick SU-8 film was spin-coated on top of the existing SU-8 film at a spin speed of 1000 rpm. The exposures for 2D and 3D were done using a 532 nm

Nd:YAG laser with an intensity of 1.5 W for 5-10 seconds to give a total exposure dose of 8-15 J/cm^2. After baking the 8μm-thick film at 65 ℃ for 5 min, the resultant cationic photopolymerization only takes place in regions that were exposed to high intensities of light. The uncured regions were developed away in PGMEA (propyleneglycol monomethylether acetate) followed by CO_2 supercritical drying to yield the 2D and 3D porous photopatterned structures.

Preparation of 2D and 3D polymer particles: Exposures were done using a 532 nm Nd:YAG laser with a varied intensity of 1.3-1.4 W for 4-8 seconds to give a total exposure dose of 6-11 J/cm^2. After baking the 0. 8 μm-thick film for the square and 4μm-thick film for the P structure at 65 ℃ for 5 min, the uncured regions were developed away first in PGMEA (propyleneglycol monomethylether acetate) and secondly in NMP (N-Methyl-2-Pyrrolidone). The film was finally rinsed with isopropyl alcohol followed by CO_2 supercritical drying to yield the lightly connected 3D polymer particles. NMP, known for its exceptional solvent power and relatively low toxicity, is readily biodegradable and can be used as substitute for methylene chloride safely and effectively in the electronic industry applications such as a photoresist stripper.

UV/ozonolysis: The ozone used was produced by a LG-7, Ozone Generator (Ozone Engineering). In this apparatus, ozone is generated by a high voltage discharge between ceramic and metal electrodes. Oxygen is flowed into the corona discharge gap. The output of the ozone generator was fed into a glass horizontal tube containing the samples to be exposed. In conjunction with ozonolysis, irradiation was performed by using a UV lamp

(BlueWave™ 200, Part number 38905, $\lambda=254$ nm) mounted in a quartz tube that provided a power of approximately 7 W/cm^2 at 1 cm distance from the light source. The generation of ozone by the UV lamp radiation was ascertained by iodometric titration. Upon exposure to ozone, the colorless iodide transformed to orange-red iodine (Scheme 1). The exposure was varied from 90 minutes to 120 minutes.

$$2K^+ + O_3 + 2I^- \longleftrightarrow I_2 + O_2 + O^{2-} + 2K^+ \quad \text{------ Scheme 1}$$
$$\text{colorless} \qquad\qquad \text{orange red}$$

O$_2$ plasma etching: We found disconnection of the particles by O$_2$ plasma etching for 10-12 min (Harrick PDC-32G plasma cleaner/sterilizer, radio frequency power level approx. 5.4 W) showed similar result to the one by UV/Ozonolysis.

Solidification and freeze-Drying: 2D and 3D structures were pre-wetted with ethanol and dipped into 10ml of water followed by freezing inside a liquid nitrogen chamber. After freezing, the sample is placed under vacuum to allow for direct sublimation of the water in the chamber.

Characterization: Sample morphology was analyzed with a field-emission high-resolution SEM (JEOL 6320FV).

Modeling and supporting experiments: Various volume fractions of the square (S2a, S2b, S2c, S2d) and the simple cubic structure (S2e, S2f, S2g, S2h) were obtained by plotting intensity distributions of the parent structure at different/decreasing isointensities in MATLAB®. Various etching stages/times of the structure were also obtained by performing isotropic etching time-steps on the initial structure obtained from the

exposures. Figures 2a and 2d in the manuscript are the isointensity surfaces obtained from the level-set approach for the square and simple cubic lattice, while figures 2b-c and 2e-f show isotropic etching till pinch off for the respective structures obtained. These two sets of figures may be compared to demonstrate that the simply lowering the intensity will cause significant loss of the concave multi-valency of the particles.
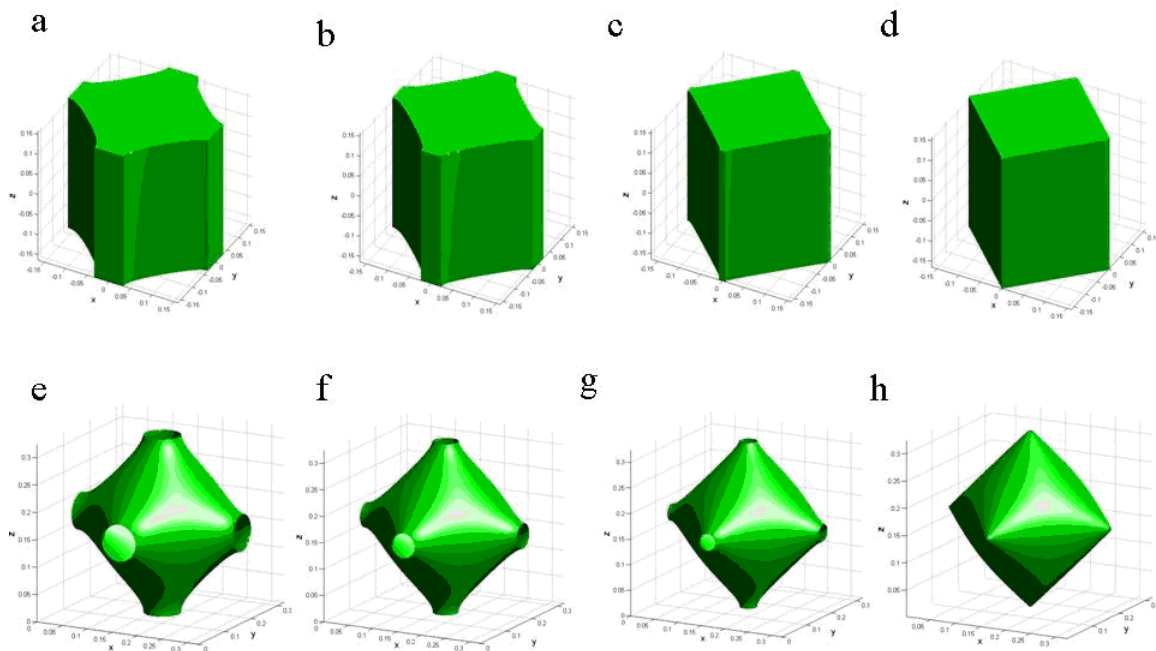

Figure S2. The theoretical model of single unit cell for the truncated rectangular prism structure (a, b, c, d) and for the simple cubic structure (e, f, g, h) at various volume fractions. Simply decreasing volume fractions along iso-intensities of the parent structure results in a loss of the distinct "valency" in the final particles.

Various volume fractions of 2D square lattices (S3a, S3b, S3c) were obtained by decreasing the light intensity and normal development in PGMEA.
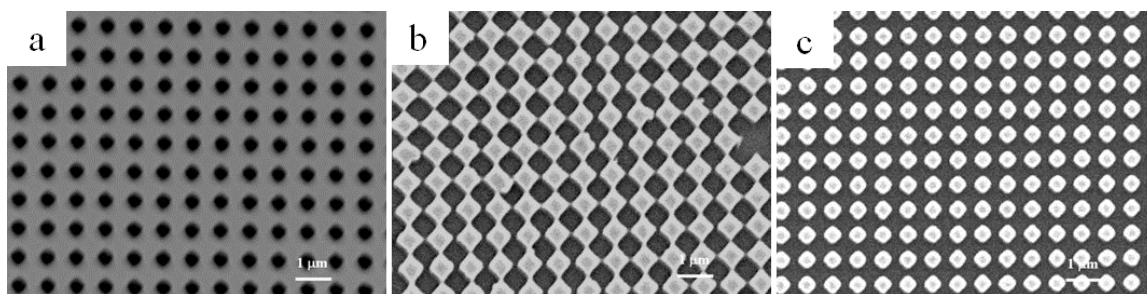
Figure S3. The experimental SEM images of 2D square lattice at different volume fractions with (a) 100%, (b) 60%, and (c) 40% of normal light intensity showing losing the distinct "valency" in the final particles.
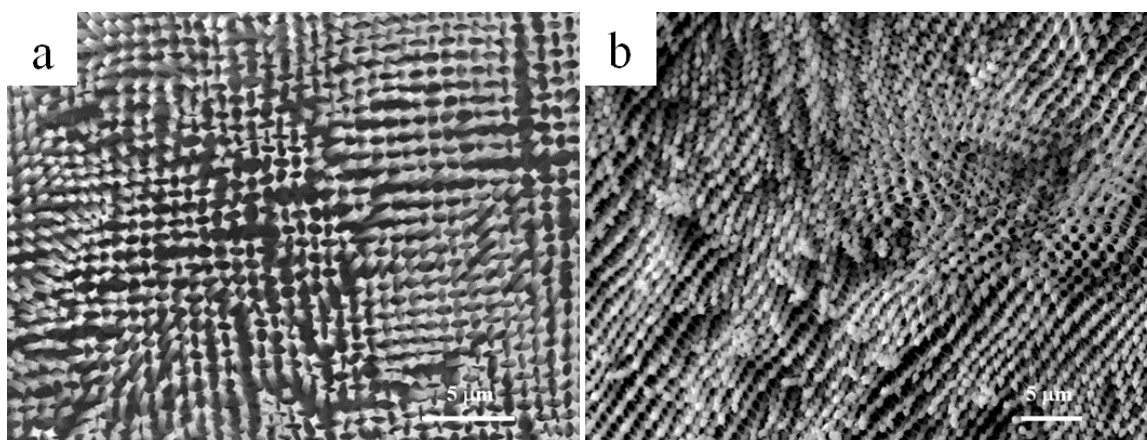

Figure S4. The large area SEM images of 2D square (a) and simple P structure (b) before pinch off by strong wet development in NMP followed by CO2 supercritical drying.