SUPPORTING INFORMATION FOR "Extraordinary Long Range Order in Self-Healing nonclose packed 2D arrays"

Stefan B. Quint^{1,2} and Claudia Pacholski^{1*}

¹Max Planck Institute for Metals Research, Department of New Materials and Biosystems, Heisenbergstr. 3, 70569 Stuttgart, Germany ²University of Heidelberg, Department of Biophysical Chemistry, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

METHODS

PolyNIPAM microgel synthesis:

Hydrogel microspheres composed of N-isopropylacrylamide (NIPAM, recrystallized from n-hexane) and N,N'methylene bisacrylamide (BIS) were prepared by an aqueous free-radical precipitation polymerization according to Pelton et al.. 23 Briefly, 0.19 mol/L NiPAM and 0.05 mol/L BIS were dissolved in 124 mL deionized water (~18.2 M Ω cm) using a 250 mL three-neck flask. The solution was heated to ~70 °C under argon atmosphere and stirred with a magnetic stir bar. The polymerization was started by injection of a potassium peroxodisulfate (KPS) solution (0.002 mol/L) and carried out for 6 hours at ~70 °C under an Ar environment. The polyNIPAM microgel was purified by centrifugation, decantation, and redispersion in deionized water (three times) and finally by filtration (Acrodisc 25 mm syringe filters with Versapor membranes, pore diameter: 1.2 µm). The diameter of the swollen poly(NIPAM) microgels is 1204 ± 64 nm estimated by scanning electron microscopy (SEM). For this purpose, we analyzed several SEM images with a total number of roughly 10000 microspheres and determined the lattice constants using the image analysis tool of ImageJ 1.37v. This size determination method is based on the assumption that the center-to-center distance of the ordered polyNIPAM discs is correlated to the diameter of the swollen polyNIPAM microspheres.23 The concentration of the polyNIPAM dispersion used in this study was determined by gravimetry. An average over three measurements yields a concentration of 19.6 ± 0.4 g/L. After filtration the polyNIPAM dispersion was diluted 1:50 (v:v) with deionized water.

Self-assembly:

PolyNIPAM microgel assembly was investigated on glass coverslips (2 x 2 cm, obtained from Carl Roth, Germany) which were cleaned with a 3:1 mixture of H2SO4 (95-98%) and H2O2 (30%) for 1.5 h followed by extensive rinsing with deionized water (~18.2 M Ω cm). Prior to spin-coating, the cleaned glass coverslips were stored in deionized water for 1 - 24 h and were blown dry with N2.

40 μ L H2O was placed on a cleaned glass cover slip and mixed with 15 μ L EtOH. Then 2.5 μ L of polyNIPAM microsphere dispersion (3.4 ± 0.4 mg/ml) was added. Right after adding the dispersion a pressure-modulated gas stream was directed to the sample surface using a nitrogen gun. Afterwards the substrate was dried by spin-coating. Spin-coating was carried out with a Laurell WS-400A-6NPP Lite spin coater and the spinning program consisted of 6 min at 500 rpm followed by 1 min at 6000 rpm using an acceleration of 100 rpm/s in both cases. In an alternative approach 40 μ L of a 1:15 diluted dispersion was placed on a cleaned glass cover slip. After addition of approximately 15 μ L EtOH the dispersion droplet divided into smaller droplets which coalesced after several seconds forming a thin liquid film on top of the glass cover slip. Subsequently a gas stream and spin coating was applied as described above. The two approaches differ in the manner that the gas stream is applied during microsphere assembly in the first case or after microsphere assembly has already taken place in the latter case. We obtain slightly better results with the first approach.

Imaging & analysis:

PolyNIPAM arrays were observed with a Zeiss Ultra 55 "Gemini" scanning electron microscope (SEM) and were coated with carbon before examination. In order to determine the homogeneity of the polyNIPAM array over large areas, 12 images were taken from 3 samples. Roughly a total number of 1050000 polyNIPAM microspheres have been investigated by this method. The lattice constant and the order parameter were determined by analysis of 30 SEM images of 3 samples using the image analysis tool of ImageJ 1.37v. Optical brightfield phase contrast images were taken with a Zeiss Axiovert light microscope using magnifications of 630x.



Figure S1: High resolution SEM image of a polyNIPAM array prepared by air-drying a thin liquid film with already assembled polyNIPAM microspheres at the interface (figure 3 a)).



Figure S2: High resolution SEM image of a polyNIPAM microsphere array fabricated by assembly of polyNIPAm microsphere at a liquid/air interface and spin-coating (figure 3 b)).



Figure S3: High resolution SEM image of a highly ordered polyNiPAM array resulting from the assembly of a polyNIPAM monolayer at the liquid/air interface by oscillatory air shear and spin coating (figure 3 c)).



Figure S4: Radial distribution function of a highly ordered non-close packed array (corresponding to figure 3 c)) demonstrating the exceptional long-range order. Green bars indicate the expected peak positions of an ideal hexagonal lattice.

In order to quantify the lattice order we calculated the pair distribution function g(r). The particle positions were located using the particle analysis function of ImageJ. g(r) was computed as follows:

$g(r)=N(r)/2\pi r\Delta r\rho$,

where N(r) is the number of particles in an annular disc of radii r and $r + \Delta r$ drawn with a particle at the centre, ρ the number of particles per cm². g(r) was averaged over about 35000 particles (the size of the used rectangular SEM image was 0.24 mm x 0.16 mm). The function is displayed in figure S4 for the first 10µm. Also shown are the expected peak positions for a perfect hexagonal lattice. The peak positions of the array coincide with the predicted peak positions. Moreover the individual peaks are quite well resolved. The first peak was least square fitted with a Gaussian function to determine the standard deviation of the lattice constant (dL). We calculated a lattice constant (L) of 1092 ± 35 nm which means that on average the particle to particle distance deviates only by roughly 3 %.

sample	lattice constant L [nm]	standard deviation dL[nm]
VV53_300909_1	1092	35
VV53_061009_1	1104	33
VV53_061009_2	1113	31
VV53_300909_1_s	1095	44
VV53_061009_1_s	1107	33
VV53 061009 2 s	1114	32

Table S1: Structural features of highly ordered arrays