Nanoscale

Supplementary Material (ESI) for Nanoscale

Supplementary information for
DOI: 10.1039/C1NR10086F

COMMUNICATION

Effect of substrate on particle arrangement in arrays formed by self-assembly of polymer grafted nanoparticles

Electronic Supplementary Information

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DOI: 10.1039/ C1NR10086F

Aqueous gold colloids of size 7 ± 0.7 nm were synthesized at room temperature using tannic acid as both reducing and stabilising agent, as reported earlier[1]. Briefly, 30 mL of 0.64 mM aqueous chloroauric acid was added to 45 mL of 0.9 mM aqueous tannic acid dropwise. The pH of the reaction mixture was always maintained above 6.4 by the addition of requisite amounts of 1 % (w/v) KOH solution intermittently. Polymer grafting to gold nanoparticle was achieved by mixing 7 mL acetone solution (containing 0.02 % (w/v) thiol terminated polystyrene, molecular weight: 20000 g/mol, Polymer Source Inc.) with 5 mL of aqueous gold colloid. The solution was left undisturbed overnight, and then centrifuged at 3500 rpm for 30 minutes. The precipitate was then washed with 5 mL acetone twice to remove excess thiol terminated polystyrene molecules. The final precipitate was re-dispersed in the desired organic solvent prior to fabricating nanoparticle arrays. Thermo Gravimetric Analysis, TGA (Perkin Elmer, Pyris6000) measurements indicated that the nanoparticle surface is saturated with polystyrene thiol after this procedure, with the thiol coverage corresponding to 1.57 molecules/nm^2. p-type silicon substrate (with native oxide) was cleaned using standard RCA method[2], followed by UV-Ozone cleaning using a commercial UVO cleaner® (Jelight-42). Graphite substrates (~ 100-200 nm thick) were generated by cleaving a graphite block with scotch-tape. HPLC grade organic solvents were used as received without any further purification. Deionized water from a Millipore Milli-Q® system was used throughout.

Field-Emission Scanning Electron Microscope (FESEM) images were obtained using Ultra-55, Zeiss NTS GmbH, at an operating voltage of 10 KV. Multiple images taken at different locations were used for image analysis. The interparticle spacing, i.e. the distribution of the edge to edge distance of nearest neighbours (for >100 particles across several images from different areas of the film), is determined using a customised code written in IGOR Pro™ environment. In the case of the samples formed on the graphite substrate and polystyrene thiol modified water surface, the vacancy defects were higher and resulted in bimodal curves; the values reported in the text are for the dominant mode. The standard deviation of these distributions are in the range of 1-2 nm, which is reasonable given the errors associated with thresholding[3] and the resolution of the FESEM. Zetasizer Nano (Malvern Ltd.) was used for DLS measurements. AFM characterization was performed using MFP-3D (Asylum Research) in a clean room environment, maintained at 21°C and 45 % RH. A set of silicon nitride tips (Olympus, OMCL-AC-240 TS, spring constant: 20-40 N/m, resonant frequency: 340 kHz) were used for imaging and force spectroscopy. The heights of the nanoparticle films were obtained by averaging across several cross-sections from images spread across the sample (typically several mm's across), and the standard deviations of the measured values (n>100 cross-sections) were approximately 1 nm. The force-displacement curves reported were repeatable across several areas, and were further verified by intermittently checking the reproducibility of force-displacement curves on bare silicon substrate. In the case of the array formed on polystyrene thiol modified water, the force-displacement curves were almost identical everywhere on the substrate, except for reproducible differences in adhesive force, due to transfer printing of the polystyrene thiol layer along with the nanoparticle array. This was further confirmed by the phase image of the sample, which showed that the phase lag was similar both on top of the array and on the 'reference' plane (Fig. S3).

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The attractive component for ordering nanoparticles is provided by capillary immersion forces. The limiting form of the capillary immersion energy between two equal sized spherical particles of size R is given by (proposed by Paunov and coworkers[4]),

$$\Delta W_{cap} = 2\pi\gamma Q^2 ln(1.78qL/2) \quad (1)$$

where, γ, L, Q and q^{-1} represent the solvent surface tension, centre to centre distance of the particles, capillary charge of the particle (~ 0.7R), and the capillary length respectively. The capillary length is defined by the following relation

$$q^2 = (\Delta\rho g - \Pi'/\gamma) \quad (2)$$

where, $\Delta\rho$ represents the density difference between nanoparticle and solvent. For thick films, the disjoining pressure component can be neglected while for thin films, as in the current study, the derivative of disjoining pressure with respect to the film thickness l_o has to be accounted for in estimating the capillary length. The disjoining pressure is given by

$$\Pi = A_H/6\pi {l_o}^3 \quad (3)$$

where, A_H represents the compound Hamaker constant for the interaction of the substrate with air across the solvent.

Steric repulsion between two particles due to compression of polystyrene ligands is the most significant amongst the repulsive forces opposing the capillary immersion forces, and is modeled based on the simplified form[5] of the original expression proposed by de Gennes[6],

$$\Delta W_{steric} = \frac{100c\delta^2}{\pi\sigma^3} k_B T exp\left[\frac{-\pi(L-2c)}{\delta}\right] \quad (4)$$

where, c, σ, and δ represent the core radius, thiol foot-print diameter, and brush thickness respectively.

Experimental data were used for computing the interaction energy between equal sized spherical particles. Based on SEM measurements, core radius of 3.5 nm was used, while measured DLS hydrodynamic diameter was used for computing polymer brush thickness. The height measured by AFM (h) was used to obtain the best estimate of the immersion film thickness[4,7] (l_0=h/2) for computing the disjoining pressure component. Physical parameters like surface tension (26.5 N/m for tetrahydrofuran, 28.5 N/m for toluene), Hamaker constants (22×10^{-20} J for silicon, 10×10^{-20} J for graphite, and 4×10^{-20} J for water), and densities were collated from databases. Standard methods for estimating complex Hamaker constant were used[8]. The thiol footprint diameter (σ) was set to be 0.9 nm (based on TGA measurements). With these values, the variation in disjoining pressure component between silicon and water (2537 k_bT) was found to be comparable to the elastic energy required for compressing polystyrene ligands by 50 % (3267 k_bT). The variation in disjoining component between silicon and graphite was estimated to be 827 k_bT, which is comparable to the elastic energy required for compressing polystyrene ligands by 25 % (1380 k_bT). Given the approximate nature of some of the parameter values, the computed results for differences in capillary immersion energies and elastic energies, upon changing substrates, can be considered equal.

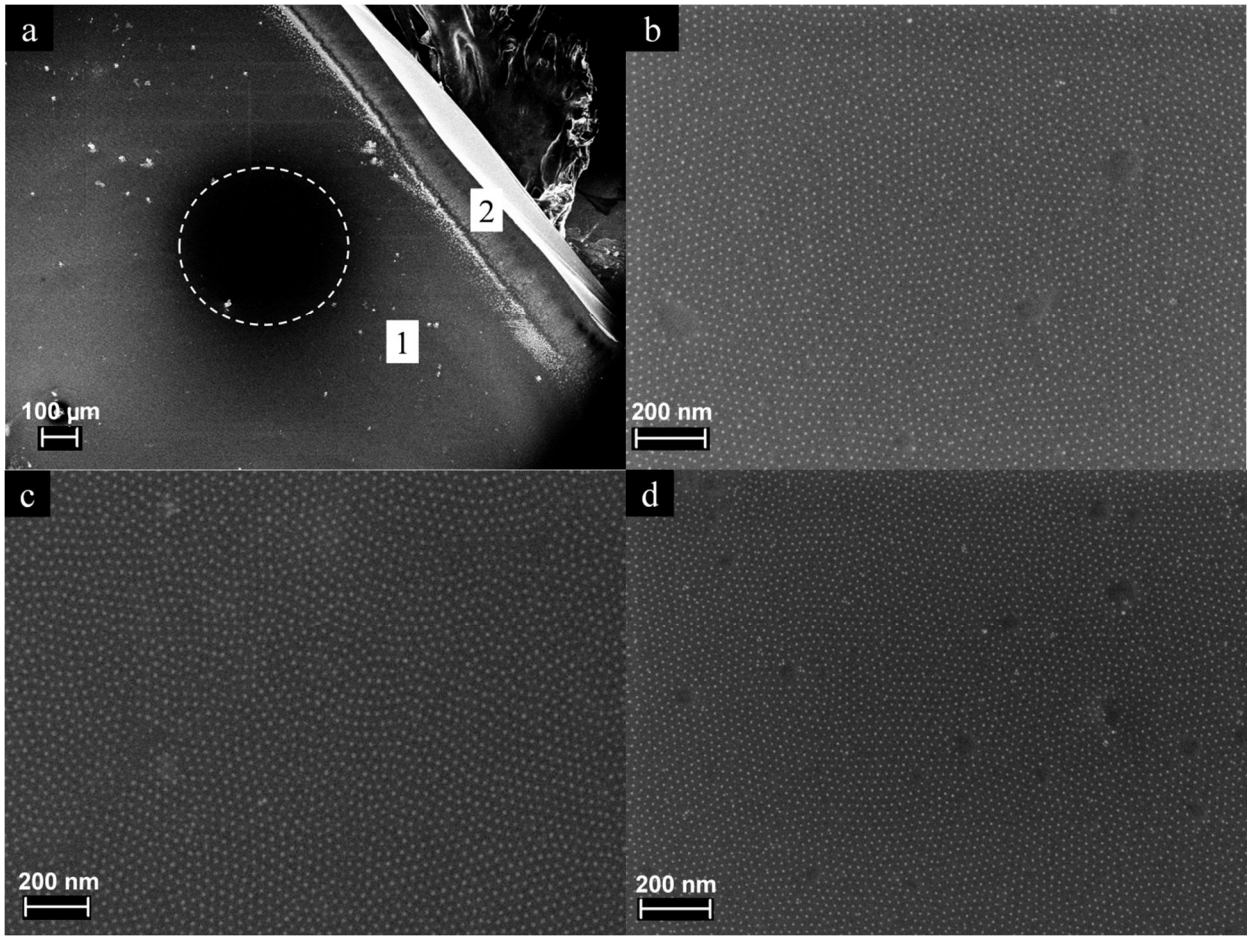

Fig. S1 Representative low magnification FESEM images of self-assembled 2D arrays formed by drop-casting gold nanoparticles from (a, b) toluene solution onto silicon substrate (with native oxide) at different magnifications, (c) toluene solution onto water, (d) tetrahydrofuran solution onto silicon substrate (with native oxide). The outlined region in fig (a) is the blind spot of the in-lens detector used for detecting secondary electrons. The regions marked 1 and 2 in (a) represent array and bare silicon substrate respectively.

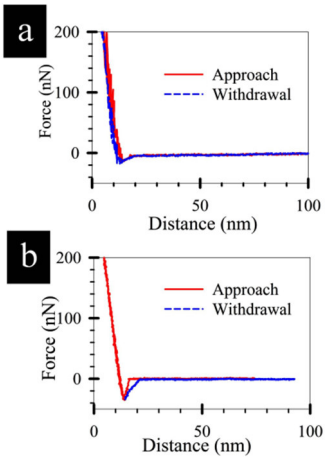

Fig. S2 Representative force-displacement curves measured on top of a (a) silicon substrate and (b) 'silicon' region presumed to be polystyrene thiol coated, due to transfer printing from water surface modified *a priori* with polystyrene thiol molecules.

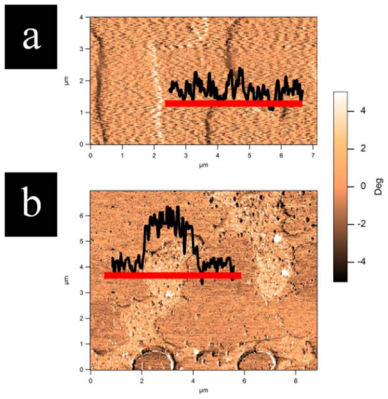

Fig. S3 Representative AFM phase scans, from the edges of self-assembled 2D arrays formed by drop-casting gold nanoparticles from (a) toluene solution onto a water surface that was *a priori* modified with a thin film of thiol functionalised polystyrene, (b) tetrahydrofuran solution onto silicon (with native oxide). The phase profiles along the length of the corresponding straight lines are shown as overlays. Negligible phase difference in fig (a) clearly suggests the transfer of polystyrene thiol molecules in addition to array from water surface.

References

1 S. K. Sivaraman, S. Kumar and V. Santhanam, *Gold Bull.*, 2010, **43**, 275.

2 W. Kern and D. A. Puotinen, *RCA Review*, 1970, **31**, 187.

3 W. D. Pyrz and D. J. Buttrey, *Langmuir*, 2008, **24**, 11350.

4 V. N. Paunov, P. A. Kralchevsky, N. D. Denkov and K. Nagayama, *J. Colloid Interface Sci.*, 1993, **157**, 100.

5 J. N. Israelachvili, *Intermolecular and surface forces*, Academic Press, London, 2007.

6 P. G. de Gennes, *Adv. Colloid Interface Sci.*, 1987, **27**, 189.

7 P. A. Kralchevsky and K. Nagayama, *Particles at fluids interfaces and membranes : attachment of colloid particles and proteins to interfaces and formation of two-dimensional arrays*, Elsevier, Amsterdam; New York, 2001.

8 V. A. Parsegian, *Van der Waals forces a handbook for biologists, chemists, engineers, and physicists*, Cambridge Univ. Pr., Cambridge, 2006.