Supporting information: Line Tension Action on 2D Networks of Gold Nanoparticles Obtained by the Bubble Method Deposition

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The following supporting information gives more details about the chemicals used during experiments, as well as protocols used for the production of hydrophobic and atomically smooth substrates, for the formation and the deposition of black bubbles onto the substrates. The AFM characterization is detailed and a movie showing the drainage of a surfactant black bubble completes the supporting information to the article.

Chemicals

Monodispersed gold nanospheres of diameter 9.6 nm were obtained from British Biocells International (BBInternational). The maximum variation coefficient for the diameter, as given by BBInternational, is 10%. They are well dispersed in water at a concentration of $5;7.10^{12}$ nanoparticles per mL. The cationic surfactant hexadecyltrimethyl ammonium bromide $C_{16}H_{33}N(CH_3)^+$ Br^- (CTAB) is obtained from Sigma-Aldrich and used without further purification. Calcium chloride ($CaCl_2$) was purchased from Sigma and used without further purification. All solutions were prepared in ultrapure water (18.2 MΩ, Milli-Q system).
Adding calcium chloride, because of its hydration properties, rigidifies the surfactant layers, which makes film transfer easier.[3, 6] Unless mentioned otherwise, the concentrations are always kept constant and equal to: gold colloids = $5;7.10^{11}$ particles/mL, CTAB = 20 mmol/L and $CaCl_2$ = 1 mmol/L. The color of the solution is an indicator of the dispersion of the gold nanospheres: if the solution is ruby-red colored, the nanoparticles are well dispersed; if the solution takes a purple tint, the nanoparticles are aggregating. In the solutions used in our experiments, the nanoparticles are always well dispersed.

Hydrophobization of substrates

The substrates used were 2-in.-diameter n-type Si (111) wafers (1-20 cm), which were 280 mm thick, provided by Neyco SA (France). Silicon substrates were etched using a 40% NH4Fsolution. For etching, substrates were first degreased in acetone and then rinsed with Milli-Q water, ethanol and Milli-Q water again. They were then cleaned in a mixture of concentrated sulfuric acid and 30% hydrogen peroxide solution (volume ratio 3:1) for 30 min to remove any organic contaminant. After being rinsed again with Milli-Q water, the wafers were placed in a 40 % NH4F aqueous solution for 10 min and were quickly rinsed afterward with ultrapure water. The ammonium fluoride solution had been first de-oxygenated by bubbling argon through the solution for at least 30 min. The silicon wafers were then re-oxidized by placing then in a mixture of concentrated sulfuric acid and 30% hydrogen peroxide solution (volume ratio 3:1) for 10 min. This step ensures the fabrication of an oxidation layer of well-known thickness and chemical nature. [1] The wafers were then etched a second time by plunging them in a de-oxygenated 40% NH_4F aqueous solution for another 10 min. They were then quickly rinsed with ultrapure water and dried with nitrogen gas. This treatment produces atomically smooth Si (111) surfaces with silicon monohydride terminations oriented normal to the surface. [1, 2, 7, 8, 9, 10, 11, 12,] NH_4F (40%) in aqueous solution and hydrogen peroxide (30%) in aqueous solution were purchased from Sigma and used as received. Acetone is ACS grade and used as received.

Transfer of bilayers onto hydrophobic substrates

The experimental cell used for transferring the black films is described elsewhere. [4, 5]

Fig. 1 shows a simplified sketch of the deposition method. A bubble is created using a plastic pipette from a surfactant solution. It is then carefully deposited onto a solution-soaked filter paper placed in a closed chamber containing the solid substrate to be used for film transfer. The filter paper is cleaned thoroughly before use in boiling ultrapure water. The bubble then drains until it becomes transparent at the top (see movie). The drainage time depends mainly on the dampness of the filter paper. It should be wet enough for the bubble to be stable but not so wet that the drainage would not be too slow. Once the film becomes black, the hydrophobic substrate is brought into contact with the bubble. The adhesion of the film to the substrate is immediate. The bubble usually breaks rapidly. The transferred film can then be characterized. The area of the surfactant film in contact with the substrate is on the order of a few square millimeters and can be easily adjusted by injecting more air and forming a larger bubble.

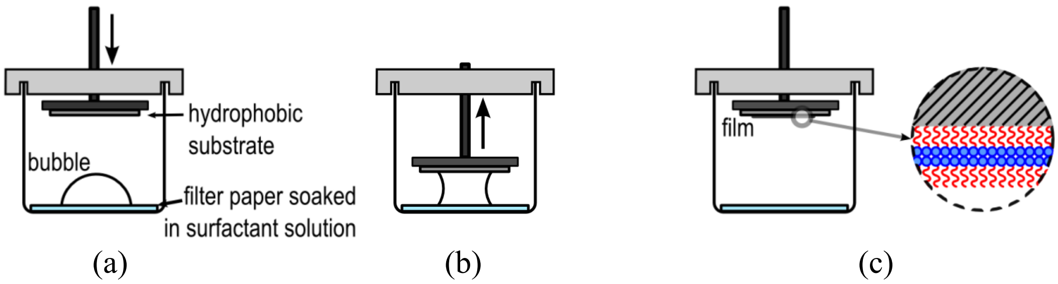

Fig. 1 A simplified sketch of the apparatus used to transfer surfactant bilayers onto a hydrophobic substrate. a) A sheet of clean filter paper is soaked in a surfactant solution. It is placed in a closed chamber of glass containing the treated solid substrate. A bubble is formed using a plastic pipette from a surfactant solution and carefully placed onto the filter paper. It is then left to drain the water. b) When the bubble is black, the solid substrate is lowered until it touches the top surface of the bubble. Due to the adhesion to the solid substrate, a cylinder forms for a few seconds during the deposition. c) The solid substrate is then removed from the chamber. A bilayer of surfactants is deposited onto its surface.

Movie caption

Drainage of a surfactant black bubble. The movie was accelerated 10 times compared to real time.

Atomic force microscopy

AFM topographic imaging was done with a Pico Scan II model AFM from Molecular Imaging equipped with silicon nitride tips mounted on silicon nitride triangular cantilevers of length equal to 300 μm and of spring constant equal to 0.03 N/m (manufacturer specifications, Nanosensors). The AFM was operated in contact force mode only. We were using WSxM software from Nanotec for the image processing which consists only in removing black ground plane or line [13]. The values of the A/P ratio were determined with the same software. The threshold for identification of the islands was fixed at 9.1nm depending on the image.

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