Supplementary figures

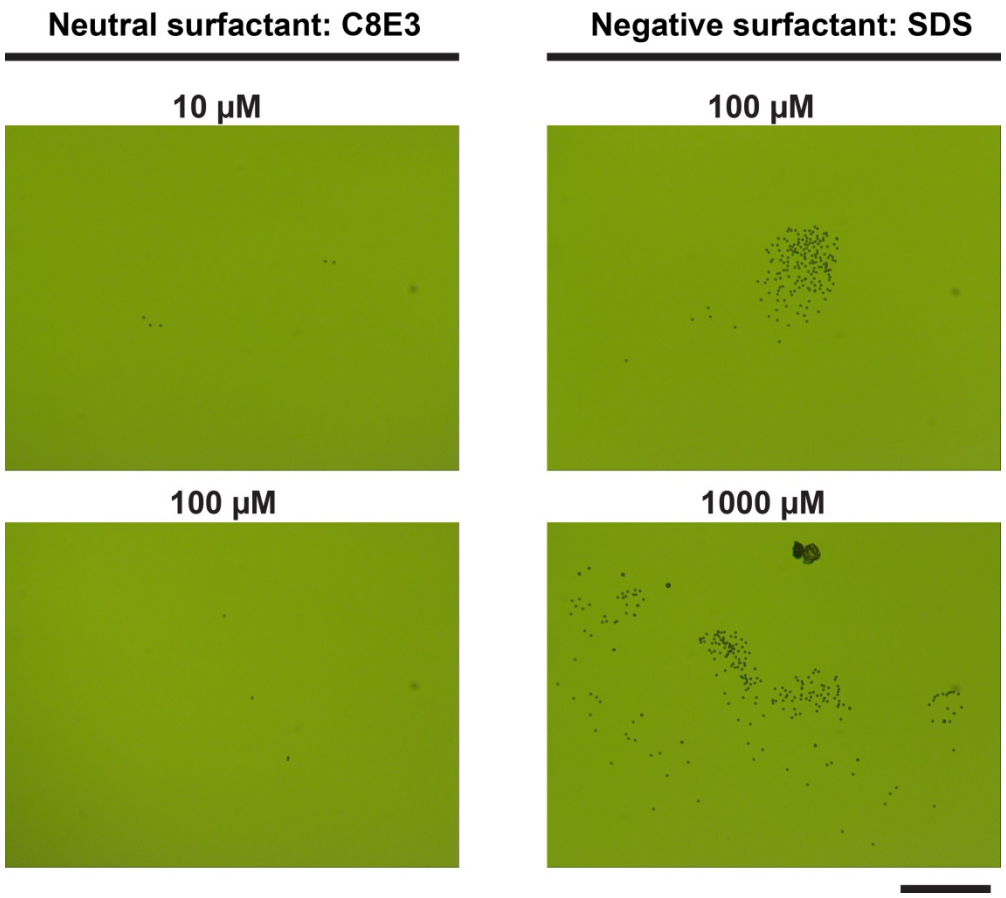

Figure S1. Brightfield transmission microscopy images of the air-water interface for a suspension of 0.05 mg/mL CML particles and different amounts of the neutral surfactant triethoxy monooctylether (C8E3, left column), or of the negatively charged surfactant sodium dodecyl sulfate (SDS, right column). In all cases the invers method has been used, and the higher concentration per surfactant is the maximum amount of surfactant that can be added without having depinning of the contact line, and leakage of the solution, while turning the well upside down. Scale bar: 200 µm.

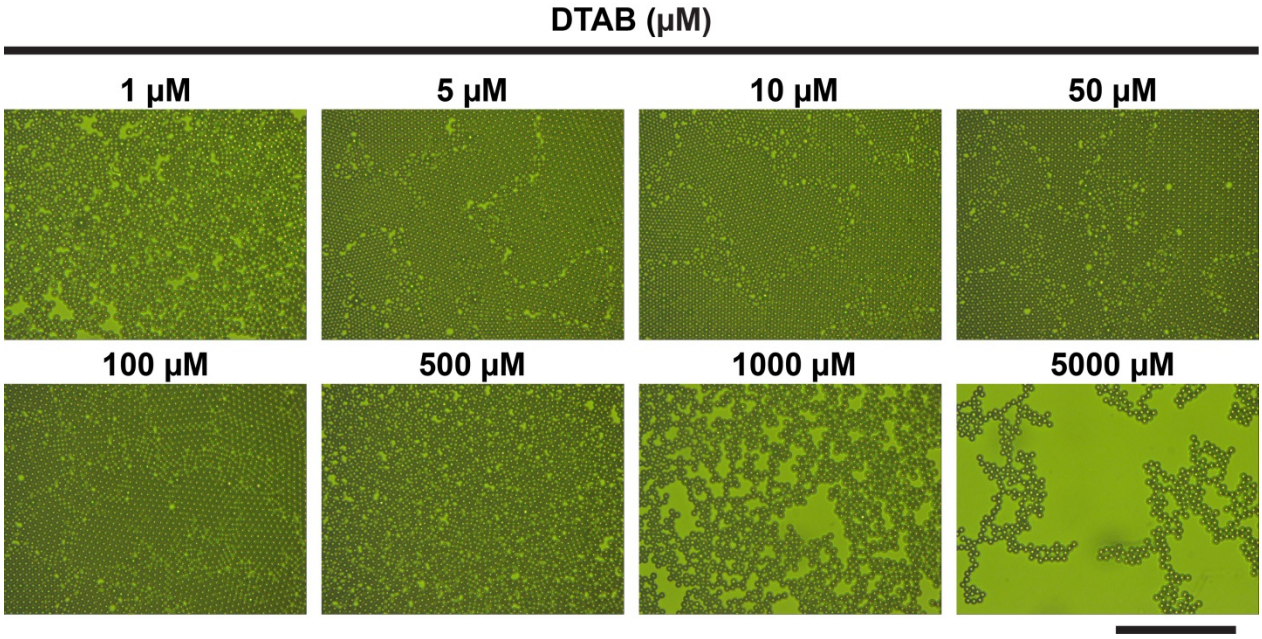

Figure S2. Evolution of the microstructure of the 2D colloidal assemblies obtained with the inverse method versus C_s, as evidenced by brightfield transmission microscopy high magnification images of the centre of the interfacial assemblies shown in Figure 1C. The particle concentration was fixed at C_p = 0.05 mg/mL. The RDFs curves shown in Figure 2B are obtained from these images. Scale bar: 100 μm.

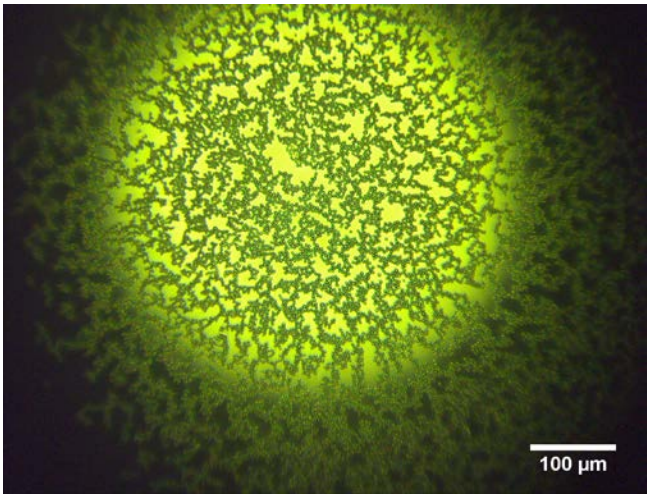

Figure S3. Brightfield transmission microscopy image of the 2D colloidal assembly at the air-water interface, obtained with the inverse method, from a suspension of 0.01 mg/mL Amidine, positively charged, polystyrene particles (diameter: 3.3 μm) in pure water.

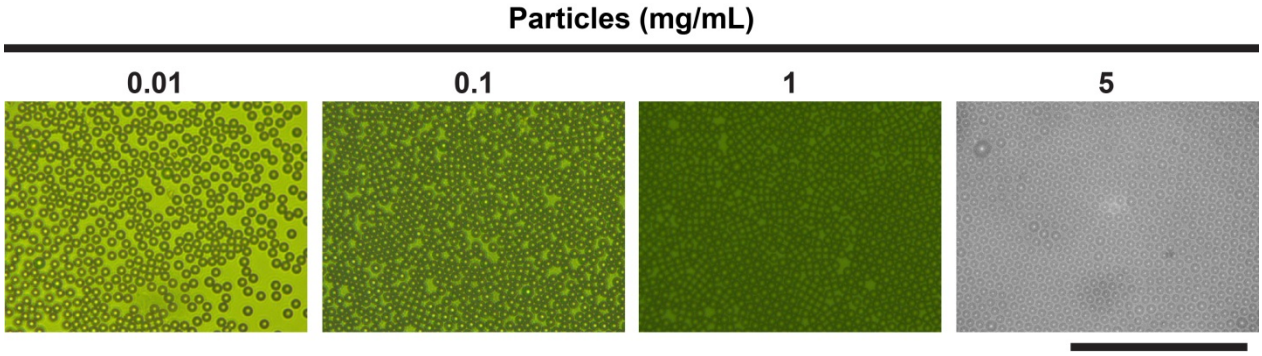

Figure S4. Evolution of the microstructure of the 2D colloidal assemblies obtained with the inverse method versus C_p, at fixed surfactant (DTAB) concentration of C_s = 1 μM. High magnification images of the centre of the interfacial assemblies obtained using brightfield transmission microscopy (C_p = 0.01 – 1 mg/mL) or reflection microscopy (C_p = 5 mg/mL) in case that the particles deposited at the bottom cause blurring of the transmission image. The number of particles adsorbed at the interface and microstructures organization (RDFs curves), are shown in Figure 3. Scale bar: 100 μm.

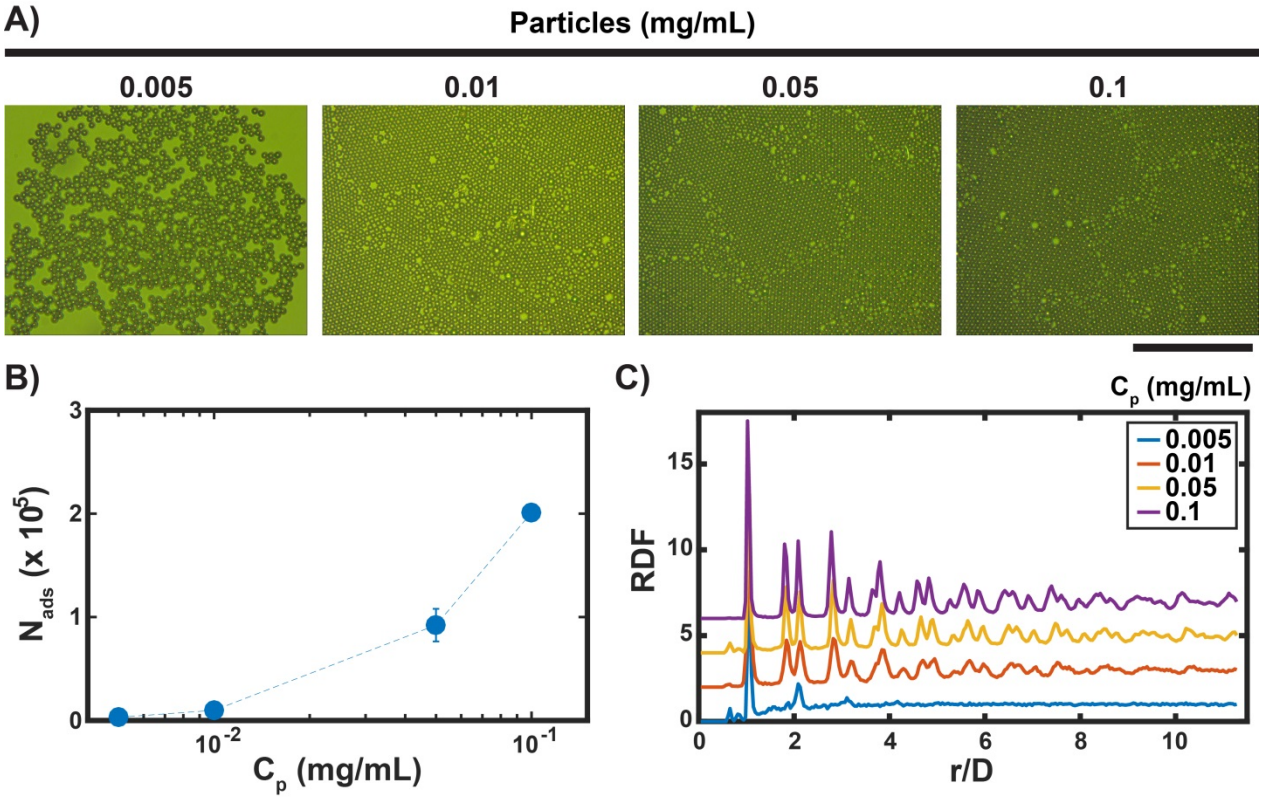

Figure S5. (A) Evolution of the microstructure of the 2D colloidal assemblies obtained with the inverse method versus C_p, at fixed surfactant (DTAB) concentration of C_s = 10 μM. High magnification images of the centre of the interfacial assemblies obtained using brightfield transmission microscopy. (B) The number of adsorbed particles (N_{ads}) at the LG interface (C_s = 10 μM), versus particle concentration (C_p), as obtained from the inverse experiment. Symbols and error bars show mean values ± standard deviations from 3 individual experiments. (C) The radial distribution functions (RDF) computed from the images in

(A); *r* is the interparticle distance, *D* is the particle diameter. The RDF are vertically offset for clarity. Scale bar: 100 µm.

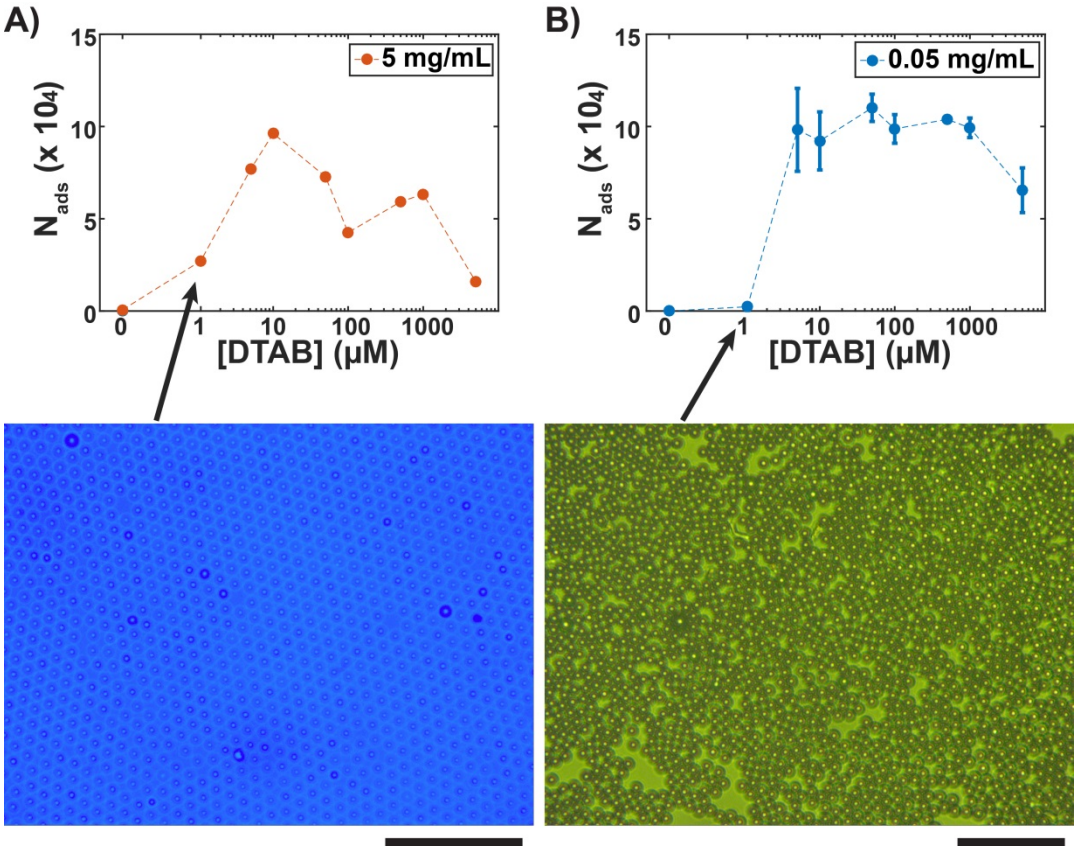

Figure S6. (A) The number of adsorbed particles (N_{ads}) at the LG interface versus surfactant (DTAB) concentration (C_s), at fixed particles concentration (C_p = 5 mg/mL), as obtained from the direct experiment. At the bottom high magnification image of the centre of the interfacial assembly at C_s = 1 µM obtained using reflection microscopy, showing a microstructure composed of particles arranged in a close-packed hexagonal lattice ($N_{ads} \approx 2.7 \times 10^4$). (B) The number of adsorbed particles (N_{ads}) at the LG interface versus surfactant (DTAB) concentration (C_s), at fixed particles concentration (C_p = 0.05 mg/mL), as obtained from the inverse experiment. At the bottom high magnification image of the centre of the interfacial assembly at C_s = 1 µM obtained using brightfield transmission microscopy, showing a microstructure composed of mostly disordered particles organized in a relatively dense arrangement ($N_{ads} \approx 2.3 \times 10^3$). Scale bar: 50 µm.

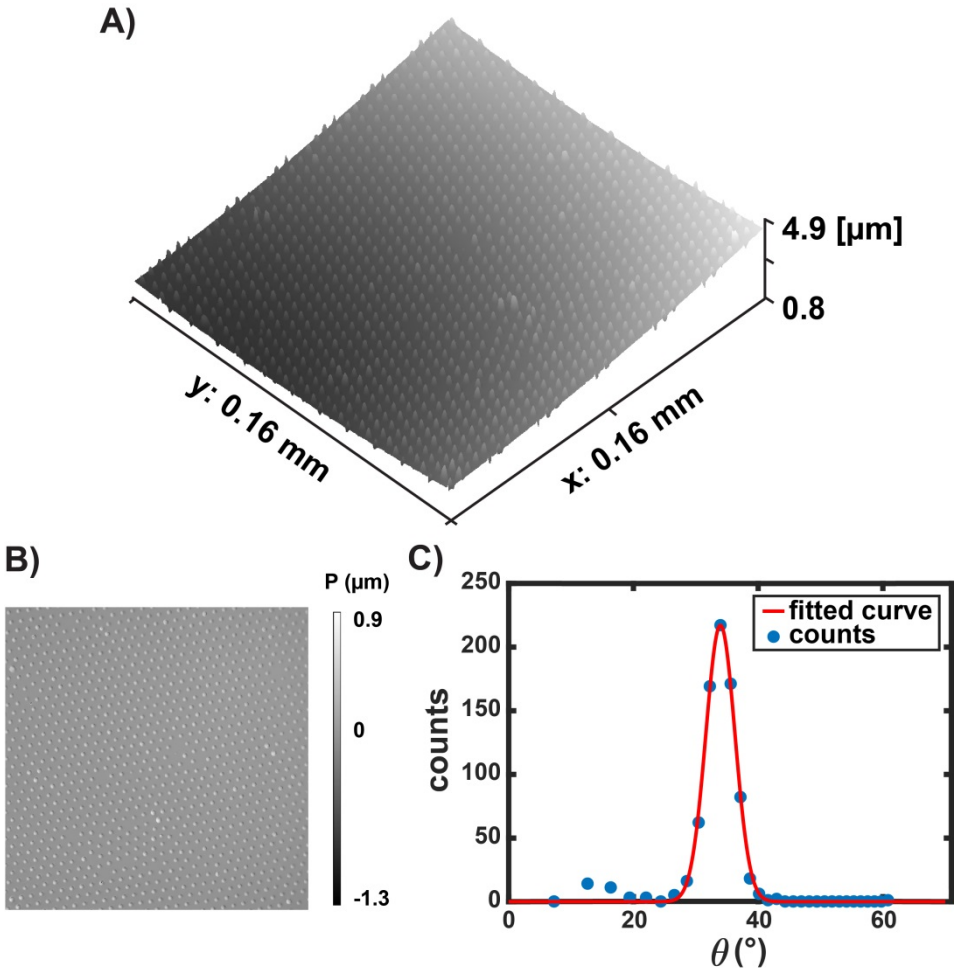

Figure S7. Calculation of the particles contact angle (θ) from fast confocal reflection microscopy at the air/water interface.

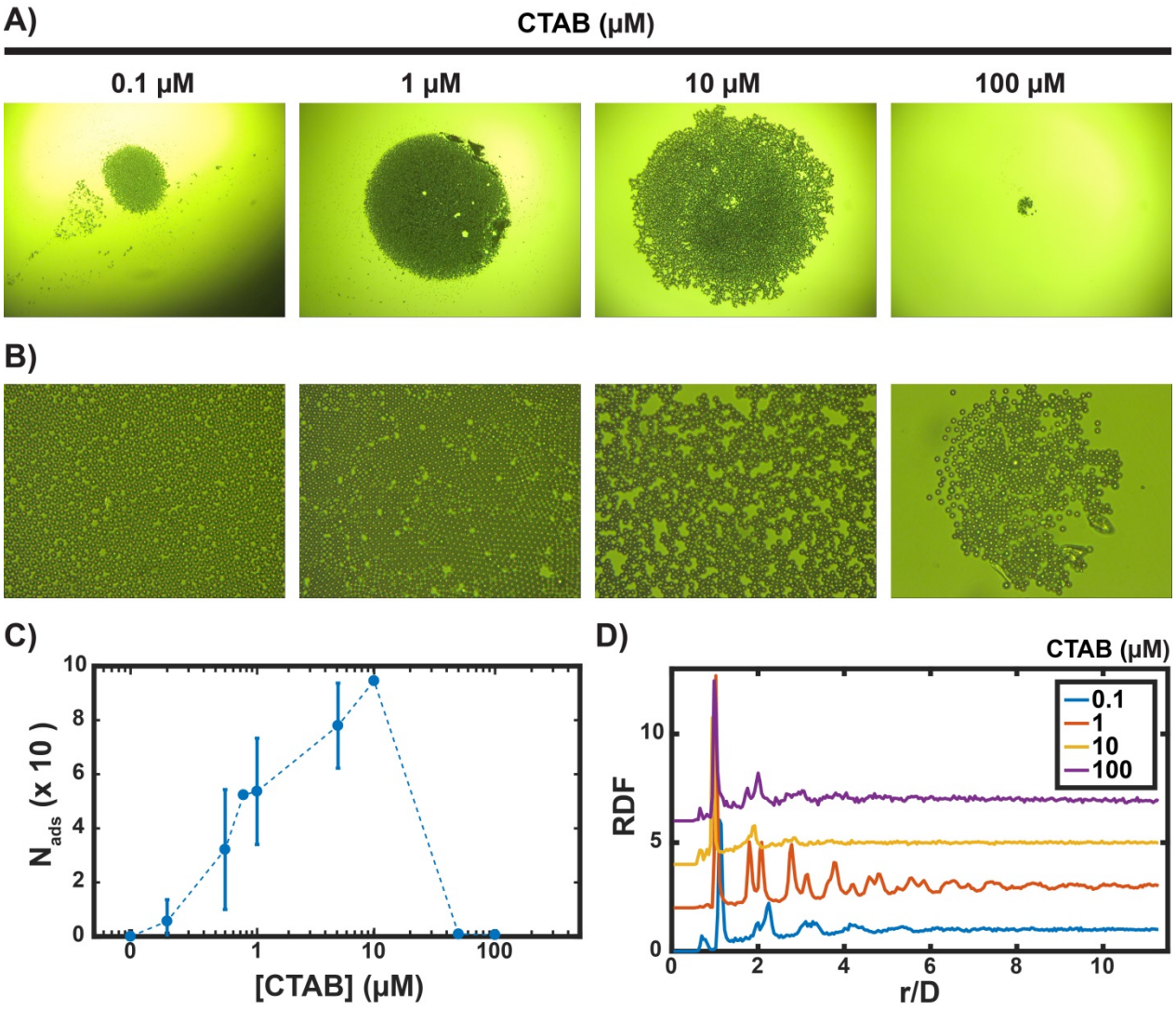

Figure S8. Nads vs. Cs for PS/CTAB + microscope images as obtained using the inverse method.

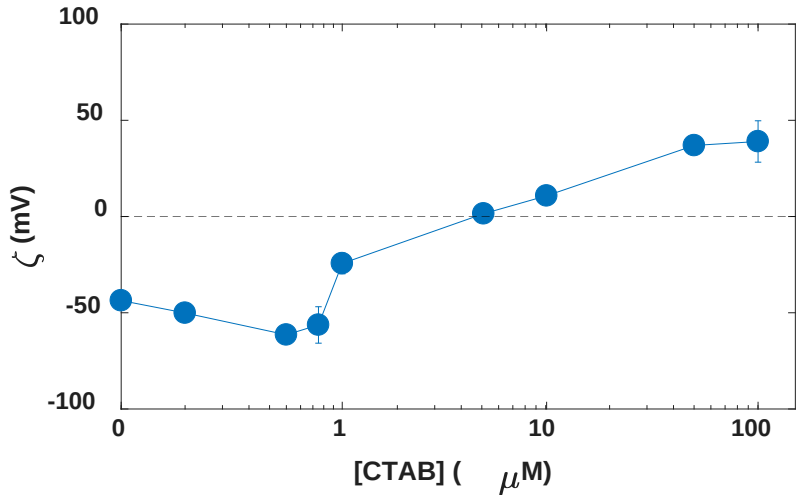

Figure S9. Zeta potential for Cp = 0.05 mg/mL as a function of CTAB concentration.

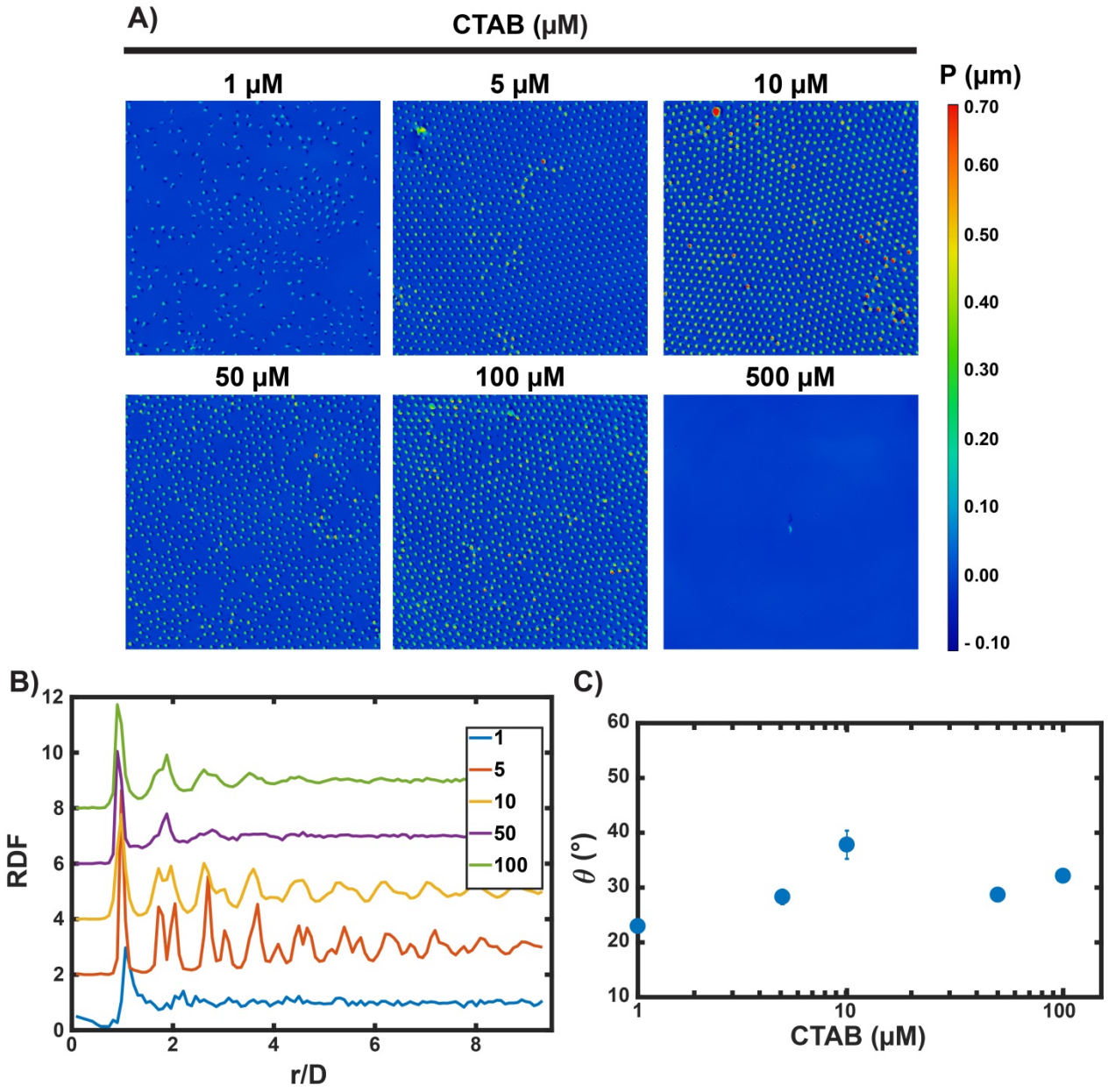

Figure S10. PS/CTAB continuation: theta (confocal) results, therefore direct method.

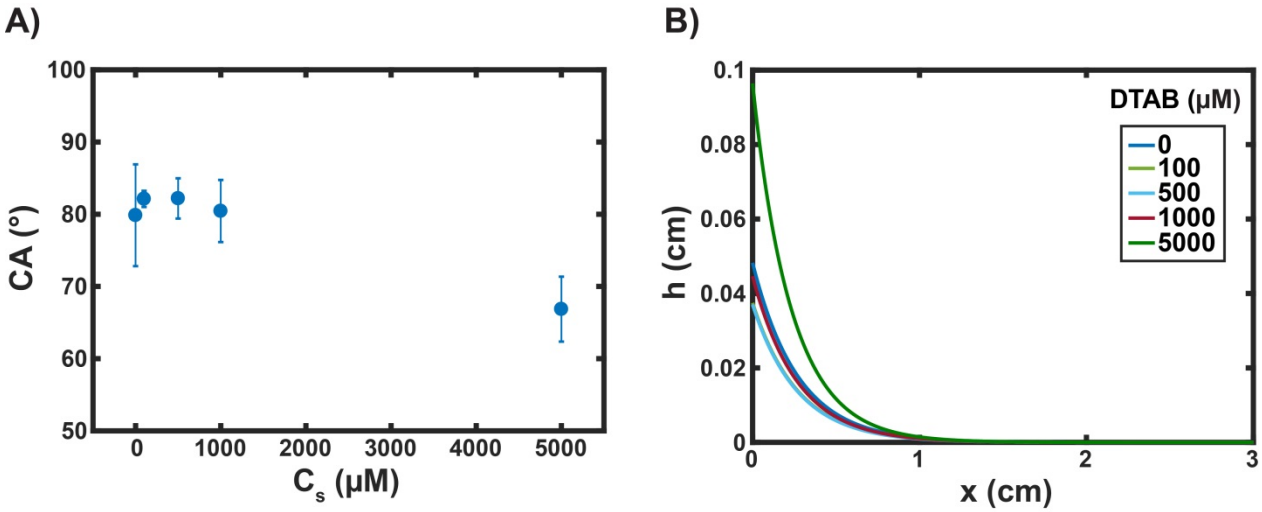

Figure S10. (A) Static contact angle (CA) of drops of solutions at various DTAB concentrations (C_s) deposited on the bottom of the Nunc chambers used for the experiments with particles adsorbed at the interface. Symbols and error bars show mean values ± sd from at least 4 individual experiments. (B) Numerical solution of the shape of the meniscus (h), for solutions at various DTAB concentrations, in contact with a vertical wall positioned at x = 0. The shape was computed knowing the experimental values for the contact angle of the solution and the surface tension values from ref XX.

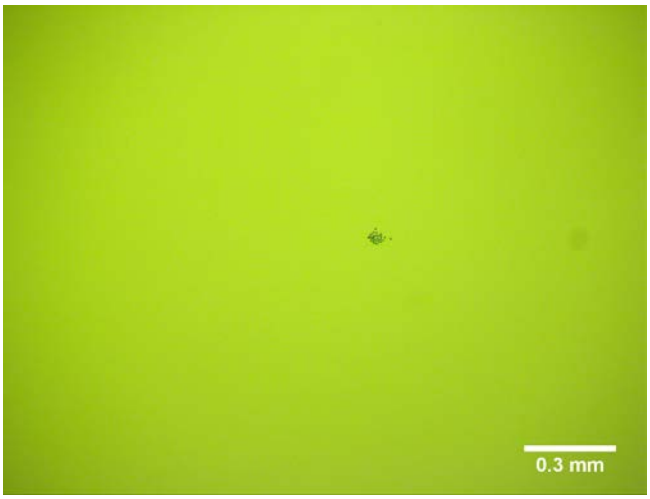

Figure S11. Brightfield transmission microscopy image of the air-water interface for a suspension of 0.05 mg/mL silica microparticles (diameter: 4.62 μm) in pure water, as obt.

Movie legends

Video S2. Polystyrene particles crystallization process at the air/water interface. The sample consists of CML anionic particles (0.05 mg/mL) and DTAB (10 μM). The video was acquired using a normal microscope (5X objective) with transmission light, focussing at the air/water interface in the centre of the well. After 1.20 seconds the x,y stage was moved to better centre the well. The actual movie duration is 300 minutes (at 90 seconds per frame), and the video starts in around one minute after placing the well below the microscope. Scale bar: 0.2 mm.

Video S3. Particles aggregation process at the air/water interface in the case of "sticky", neutralized, polystyrene particles. The sample consists of CML anionic particles (0.05 mg/mL) and DTAB (1000 μM). The video was acquired using a normal microscope (5X objective) with transmission light, focussing at the air/water interface in the centre of the well. The actual movie duration is 180 minutes (at 80 seconds per frame), and the video starts in around one minute after placing the well below the microscope. Scale bar: 0.2 mm.

Video S4. Silica particles crystallization process at the air/water interface. The sample consists of anionic silica particles (0.05 mg/mL) and DTAB (5 μM). The video was acquired using a normal microscope (5X objective) with transmission light, focussing at the air/water interface in the centre of the well. The actual movie duration is 20 minutes (at 4 seconds per frame), and the video starts in around one minute after placing the well below the microscope. Scale bar: 0.2 mm.