Supporting Information for:

From-bulk crystallization of inorganic nanoparticles at the air/water interface: tunable organization and intense structural colors

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1) Experimental Section

Materials: Ultrapure water (resistivity 18.2 MΩ·cm) was used for all experiments. All the suspensions of negatively charged silica particles, bearing silanol groups on their surface, were purchased from microParticles GmbH. They all had a density ρ = 1.85 g/cm^3 according to the manufacturer. Although the purchased suspensions were designated as pure, we followed a strict washing procedure that was found to be essential for obtaining reproducible results. A suspension of the particles at C_p = 10 mg/mL underwent typically five to six centrifugation cycles where the supernatant liquid was exchanged with ultrapure water each time. Suspensions of silver and gold nanoparticles were purchased from nanoComposix, Inc. Silver nanocubes, having a diameter of 103 ± 7 nm (coefficient of variation of diameter, CV = 6.7%), had poly(vinylpyrrolidone) (PVP) on their surface, and were dispersed in ethanol. Two gold nanospheres batches were used: one with a diameter of 100 ± 13 nm (CV = 13.2%), lipoic acid on the surface, dispersed in Milli-Q water; the other with a diameter of 99.4 ± 3 nm (CV = 3.1%), poly(ethylene glycol) (PEG)-carboxylic acid on the surface, dispersed in aqueous 2mM Citrate. Prior to each experiment, each particle suspension was mixed by vortexing (2 min), sonicated (2 min) and vortexed again for 1 min. Dodecyltrimethylammonium bromide (DTAB, purity ≥ 98%, Sigma-Aldrich) was used as received.

Samples preparation: The proper amounts of water, particle suspension and surfactant solution were added in this order to the cylindrical well (polystyrene, diameter 7 mm, Nunc Lab-Tek). Then the well was first inverted to an upside-down position, with the air/water interface being underneath the particle/surfactant mixture. The sample was left in this position for 2 h in the case of microparticles (2.4 μm diameter), 20 h for mixtures containing nanoparticles. In this position

the particles accumulated at the air/water interface due to gravity. Then the well was turned upside-down once again, with the air/water interface now being on top of the liquid, and was placed on the microscope stage where it was left unmoved for at least 6 h.

Samples for scanning electron microscopy (SEM) images were prepared as follows. We used modified chambers for achieving particles adsorption at the air/water interface. A sketch of the sample preparation for SEM images is reported in Figure S2. The bottom of the wells was cut and the wells, now open on both sides, were glued on a glass slide using an UV-curing glue. Prior to use, the glued wells were copiously rinsed with MQ water and ethanol and left for two days in a water bath in order to remove any unreacted monomer or other surface-active molecules. After loading the cells with the sample mixture, the particles were adsorbed at the air/water interface with the same protocol described above. Successively the cells were placed in a close chamber, without the coverslip on top, and slow evaporation of the water solution was allowed. Complete evaporation required around five days. Finally, the glued cells were removed, leaving glass slides with the aggregates formed at the air/water surface transferred on them for SEM imaging.

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Optical microscopy: All optical microscopy images were acquired using a home-built upright microscope, which could operate both in transmission and reflection mode. The microscope mainly consisted of a 12X Zoom Lens System (Navitar), the appropriate microscope objective (a 20×, NA = 0.42 and a 5×, NA = 0.14 for respectively high and low magnification, both from Mitutoyo) and an XYZ translation stage on which the sample cell was placed. White light illumination was provided by a flexible light guide coupled to a cold light source (KL 2500 LED,

Schott). The white light was either brought parallel to the air/water interface to enhance the visibility of the structural coloration, or it was brought from the bottom of the sample cell after passing through a diffuser and a mirror for transmission imaging, or it was inserted on a side port of the tube system of the microscope for reflection imaging (sketches of the optical set-ups are reported in Figure S1). A color CCD camera (Basler acA1600-20uc, resolution 1626 pixels × 1234 pixels, 12 bits) was used for image acquisition.

Image analysis: Quantitative analysis of the images was carried out using the ImageJ software. From the high magnification images (e.g. Figure 1B), the center of each particle in the image was detected with the "find maxima" process. Knowing the positional data of the particles enabled us to calculate the radial distribution function, which describes the number of particles sitting at a center-to-center distance *r* away from a given reference particle, using the "radial distribution function" macro.

Scanning electron microscopy (SEM): SEM images were obtained using a tabletop microscope (Hitachi, TM3000) in *EDX* mode, at magnifications ranging from 180× to 10 000×. The incident angle used was 90°.

2) Supplementary Figures

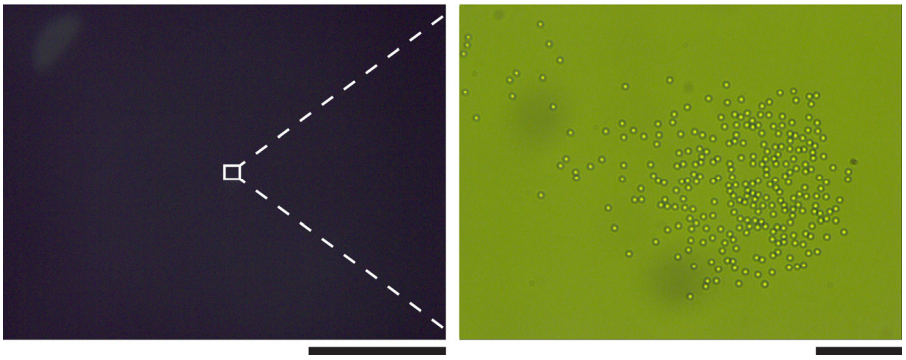

Figure S1. *Air/water interface obtained by using the "flipping method" for a suspension containing silica particles (diameter: 2.4 µm, C_p = 0.05 mg·mL-1) in pure water (no cationic surfactant addition). Left: side-light reflection microscopy image, scale bar 1 mm. Right: bright-field reflection microscopy image, scale bar 50 µm.*

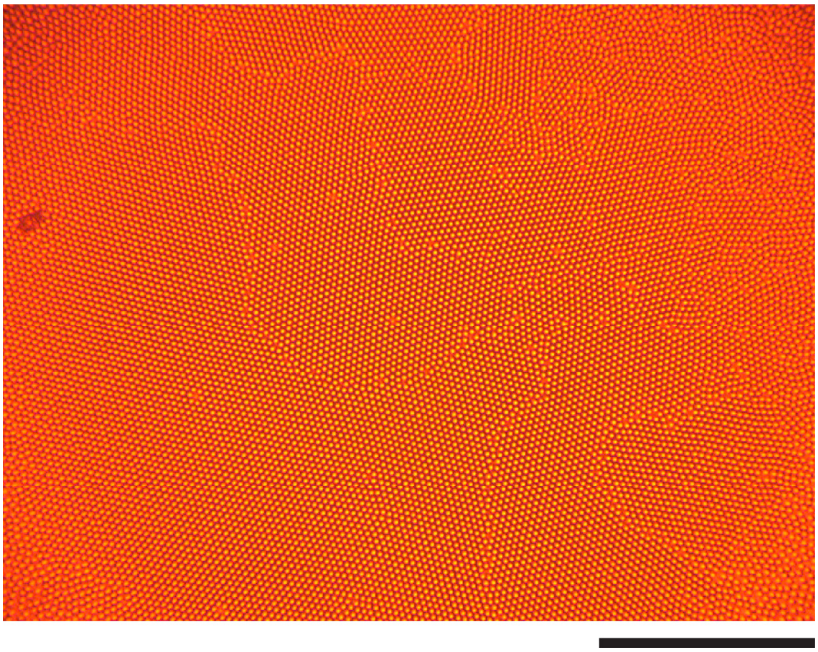

Figure S2. *Using the flipping method, silica particles (diameter: 2.4 μm, C_p = 0.01 mg·mL^{-1}) form a highly-ordered polycrystalline assembly at the air/water interface in the presence of AzoTAB (Cs = 5 μM),*[1,2] *an azobenzene-containing cationic surfactant with a CMC (12.6 mM)*[3] *similar to that of DTAB (13.4). The scale bar is 100 μm.*

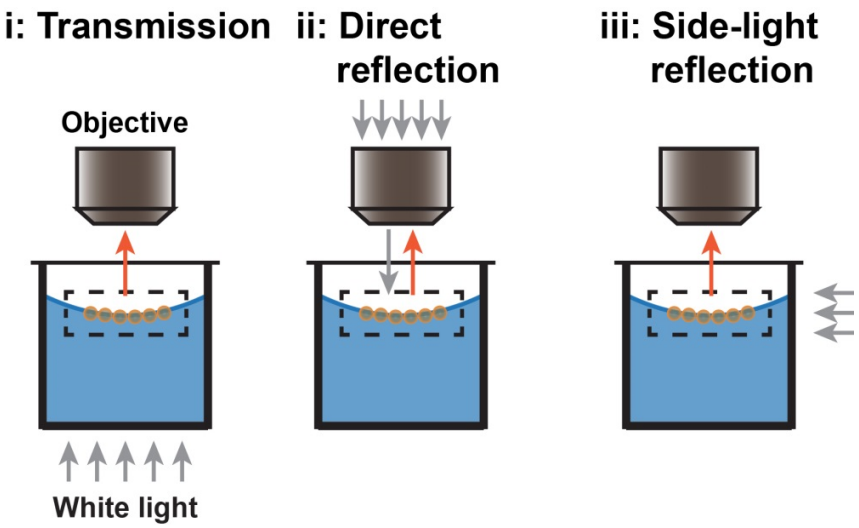

Figure S3. *Sketch of the various light configurations used for sample imaging; i: transmission microscopy; ii: reflection microscopy; iii) reflection microscopy with the white light source normal to the objective.*

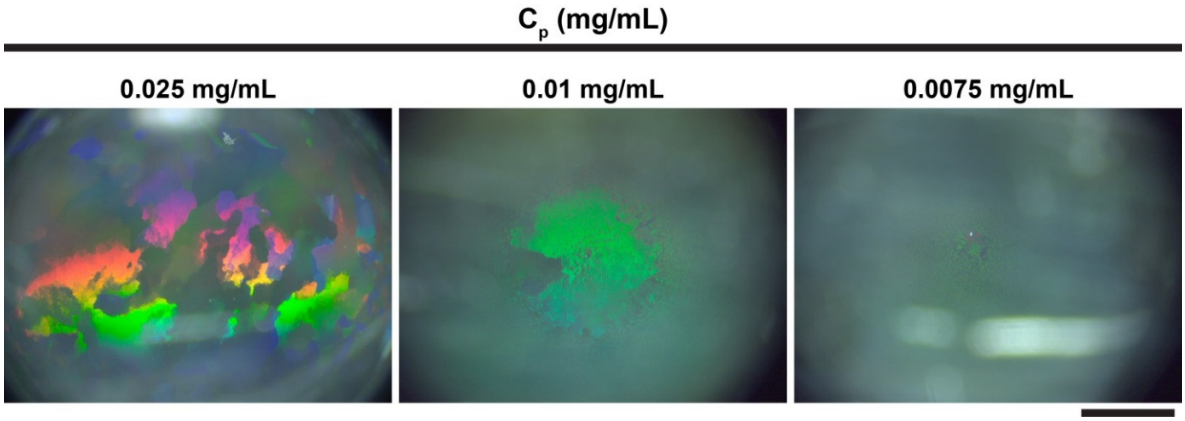

Figure S4. *Side-light reflection microscopy of assemblies of silica particles (diameter: 304 nm) at the air/water interface with C_s = 5 μM and various nanoparticle concentrations (C_p). Scale bar: 1 mm.*

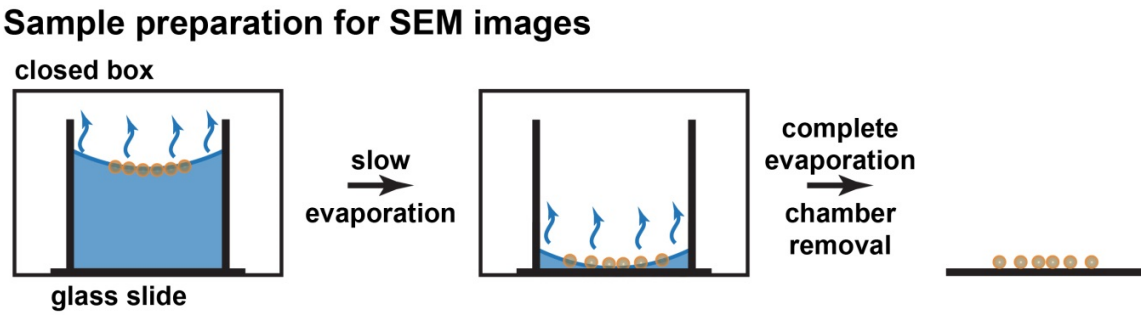

Figure S5. *Sketch of the protocol applied to transfer a particle assembly from the air/water interface to a glass slide for further imaging by SEM. The protocol is described in the experimental section. Time-lapse images showing the deposition process are reported in Movie S1.*

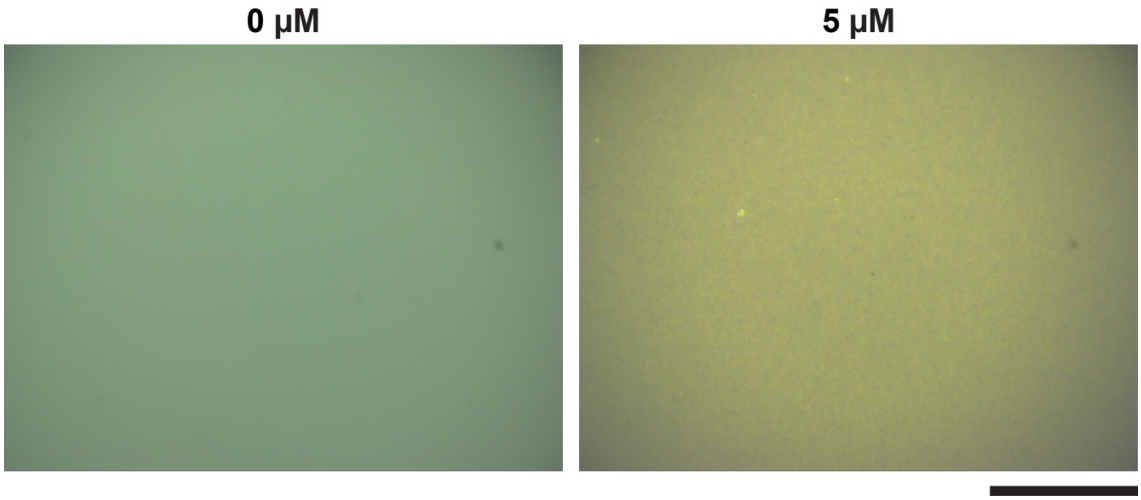

Figure S6. *Surfactant-induced adsorption of gold nanoparticles coated with lipoic acid at the air/water interface (C_p = 8 µg/mL) with C_s = 0 µM (left: no particle adsorption, weak reflectivity) and C_s = 5 µM (right, particle-covered interface, strong reflectivity). Scale bar: 100 µm.*

3) Legend of Supplementary Movie S1

Movie S1. Time-lapse bright-field microscopy images of the deposition of a 2D particle assembly from the air/water interface to a glass substrate. Silica particles (diameter: 2.4 μM) are first assembled at the air/water interface from a suspension containing C_p = 0.05 mg/mL and C_s = 10 μM. Successively, the solution is let dry inside the sample cell (see Experimental section and Figure S2). The last stage of evaporation was recorded focusing the microscope objective on the bottom solid/liquid interface, where the particles were finally collected following the evaporation of the suspension after a period of around five days. Note that the assembly deposits on the substrate from its center, and that in the last stage of evaporation liquid flows slightly perturb the particle organization within the monolayer.

4) Supplementary References

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3 A. Diguet, N. K. Mani, M. Geoffroy, M. Sollogoub and D. Baigl, *Chem. - A Eur. J.*, 2010, **16**, 11890–11896.