Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting information

Direct Visualization of the Interfacial Position of Colloidal Particles and their Assemblies

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Experimental

Colloidal assembly at the air/water interface

All of the colloids were brought to the interface according to the method described in.[52] In brief, a microscope slide, which was treated with basic piranha solution (*careful! Basic piranha solution is extremely corrosive!*) to ensure proper hydrophilicty was immersed into the water subphase (MilliQ grade water, addition of NaOH or HCl if pH was adjusted) with an angle of app. 45°. Colloid dispersions, typically around 5wt% solids content were diluted with ethanol to 50 vol% and added dropwise (app. 10 μL drops from an Eppendorf Pipette) onto the microscope glass. The colloid dispersion subsequently slides down the microscope glass and eventually comes into contact with the air/water interface. There the colloids spread rapidly due to the presence of ethanol. The glass slide allows a soft contact with the interface and eliminates mechanical disturbances, which would arise when dropping the dispersion directly onto the air/water interface. Further dispersion is continually added until the interface is completely covered with colloids. In our experiments, we use a crystallization dish with a diameter of 15 cm, which required approximately 100 μL of colloidal dispersion to cover the entire interface. In the same manner a mixture of small and large colloids in an appropriate ratio[13,54] was prepared and introduced to the interface. This ratio was chosen in a way to ensure proper 6:1 (small to large particles) stoichiometry at the interface to allow the formation of an ordered, binary LS_6 monlayer.[54]

Embedding colloids in PBCA film

To embed the colloids in the poly(butylcyanoacrylate) matrix via the gas phase, the glass dish with the crystallized colloidal monolayer at the air/water interface was carefully placed next to an aluminum dish (diameter ca. 7 cm) that was placed on a hotplate preheated to 50°C. Two laboratory jacks, one carrying the crystallization dish with the monolayer, the other carrying the hotplate with the aluminum boat were used to ensure aluminum boat and crystallization dish were level. Care was taken not to shake the crystallization dish to prevent mechanical disturbance of the monolayer. Subsequently, 200 μL of butylcyanoacrylate were added to the aluminum dish. Then, a large crystallization dish (diameter approximately 30 cm) was placed over the assembly, covering both crystallization dish and aluminum dish. After a given time, typically 2-4 hours (see Figure 2 for film thickness dependence on time), the cover and monomer-containing aluminum dish were removed to stop the process. To transfer the composite colloid-PBCA film from the air/water interface to a solid substrate, the substrate (typically a silicon wafer) was plasma treated to ensure hydrophilicity and immersed vertically into the subphase. Then, it was tilted to a horizontal position and slowly lifted. When passing through the interface, the colloid-PBCA layer was thus transferred to the substrate. After drying, samples were examined by electron microscopy (Zeiss Gemini 1530).

Optical determination of the contact angle

From the micrographs, the top view diameters of the visible parts of the colloids were evaluated using ImageJ. At least 100 objects were used for the analysis.

Colloid probe AFM

For comparison, particle contact angles were measured using an atomic force microscope (AFM), using the method described in.[46] Polystyrene particles were glued to tipless AFM cantilevers (Mikromasch NSC12) using a two-component, room temperature curing epoxy (Uhu Endfest 300). Using an AFM (JPK Nanowizard), the particles were brought into contact with the air-liquid interface of an air bubble (~0.5 μL in volume) in a polystyrene petri dish filled with distilled, deionized water, and then pulled away. Both the position of the cantilever and its deflection were recorded during the measurement. The force on the cantilever over the course of the measurement was determined from the deflection using the cantilever spring constant, which was measured using the thermal noise method[49] with a Dimension 3100 AFM. The position of the particle was determined by subtracting the deflection of the cantilever from its position. The particle contact angles were determined from plots of the force on the particle against the particle position. The receding particle contact angle were determined based on the distance d between the point where the particle makes contact with the interface and the point where the particle is at its equilibrium position with respect to the interface as the particle comes into contact with the bubble. Advancing contact angles were determined similarly, using the equilibrium position as the particle was withdrawn from the bubble. Details of the force curve calibration and contact angle calculations can be found in.[46]

Particle charge detector

The density of carboxylate groups on the particle surface was determined by titration against the oppositely charged polyelectrolyte poly(diallyldimethyl ammoniumchloride) (PDADMAC) using a particle charge detector (Mütek GmbH, Germany) in combination with a Titrino Automatic Titrator (Metrohm AG, Switzerland). For the measurement, 10 mL of the latex sample with a solid content of 1 g·L^{-1} were used. The amount of charges was calculated from the amount of consumed polyelectrolyte.

Table SI 1: characteristics of the colloids used for the studies.

Material	**Surface functionality**	***d* [nm]**	**Surface charge density**	**Preparation method**	**Ref**
Polystyrene	COOH	1063	3.1 (pH = 6)	surfactant free emulsion polymerization with subsequent seeded emulsion polymerization	[13]
Polystyrene	COOH	303	0.8 (pH = 6)	surfactant free emulsion polymerization	[13]
Polystyrene	COOH	4890±97	1.4 (pH = 4) 2.1 (p	commercial sample, Invitrogen	
Polystyrene	COOH	225	0.8 (pH=6)	surfactant free emulsion polymerization	[54]

Poly(methylmethacrylate)		350		surfactant free emulsion polymerization	
Au@PNiPAAm		300		see [11]	[11]
Silica		590		Stöber-process	

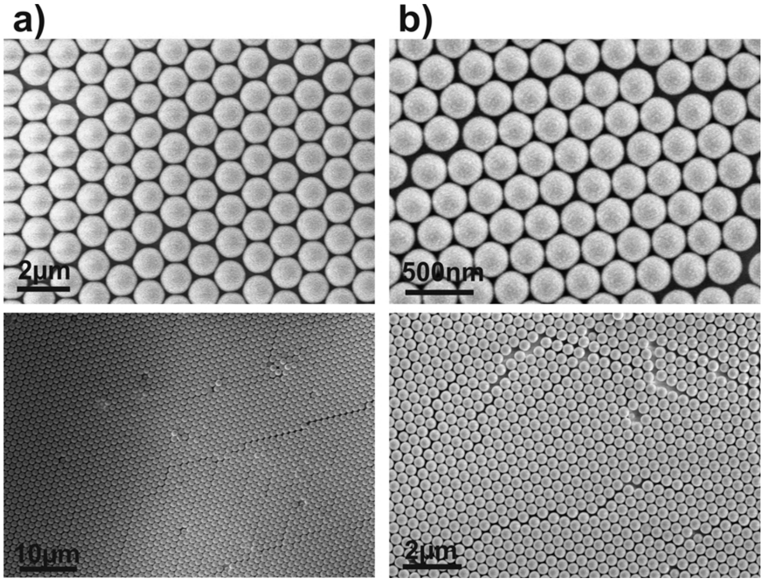

Figure SI 1: Electron micrographs of colloidal monolayers consisting of PS particles with a diameter of 1063nm (a) and 225nm (b) deposited onto a silicon wafer using a the same crystallization and transfer protocol but without contact to butylcyanoacrylate monomer show a similar crystallinity as the poly(butylcyanoacrylate) covered monolayers shown in Figure 2 of the main text.

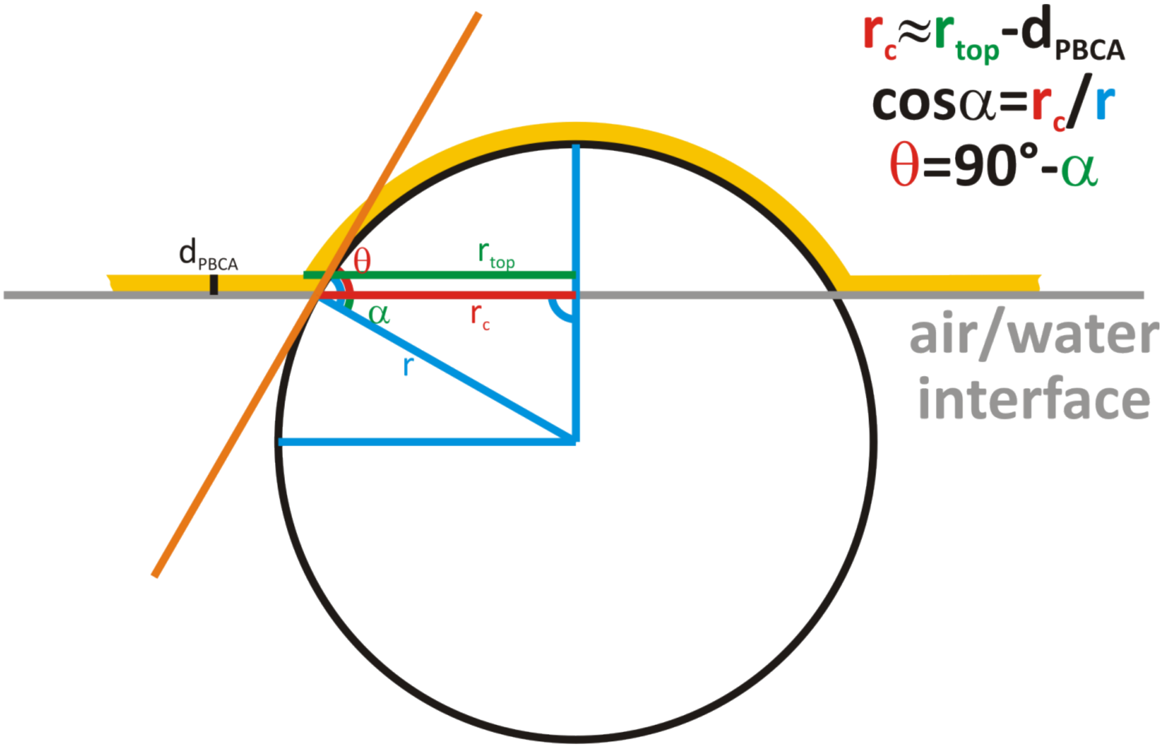

Figure SI 2: Sketch of a colloid at the air/water interface and the derivation of the equation to assess the contact angle from the top-view diameters.

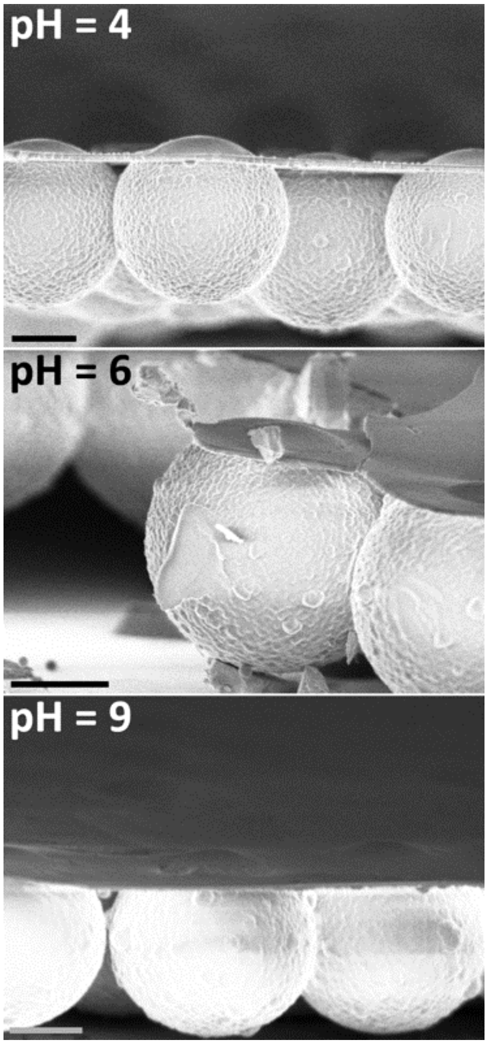

Figure SI 3: Micrographs used for the measurement of the thickness of the PBCA film. The film thicknesses are: 224 nm (pH = 4), 156 nm (pH = 6), 168 nm (pH = 9).