

Soft Janus Colloidal Crystal Film**

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Asymmetric “Janus” materials consist of objects with two sides of different chemistry or morphology. Materials such as bones and leaves as well as materials such as liquid crystals and proteins have asymmetric structures, which give unique mechanical, optical, and molecular-recognition properties. The asymmetry in Janus objects has led to novel materials as well as aggregation into interesting superstructures.^[1–5] There has been recent progress in fabrication and application of asymmetrical particles,^[2] cylinders,^[3] discs,^[4] and films.^[5]

In addition, there is a need for methods to form complex and periodical structures from colloid particles (10 nm to 10 μm).^[6] Two-dimensional (2D) colloidal crystals have been successfully used as arrays of microlenses in image processing and photolithography,^[7] as physical masks for evaporation or reactive-ion etching to fabricate regular arrays of micro- or nanostructures,^[8] and as templates for synthesis of micro- and nanostructured membranes.^[9] Introduction of asymmetry to the 2D colloidal crystals should allow for wide range of applications.

Herein, we describe a facile method to make soft Janus-type 2D colloidal crystal films using an air–water interface as a place to introduce softness, asymmetry, and regularity (Figure 1). Janus-type 2D colloidal crystal films with an area over $4 \times 10^2 \text{ cm}^2$ were fabricated. Furthermore, the synthesis of femtoliter cup arrays is described (Figure 1). The key steps of this process include: 1) synthesis of particles with controlled size, monodispersity, and shape; 2) formation of regular 2D particle arrays at the air–water interface; 3) coating of the 2D particle arrays from the aqueous phase to form Janus films (chemical oxidative polymerization of pyrrole was selected as a model reaction to coat 2D colloidal crystals facing the aqueous phase and connect the particles in a continuous film); 4) removal of the particles from the Janus film by dissolution in a solvent to form a 2D femtoliter cup array.

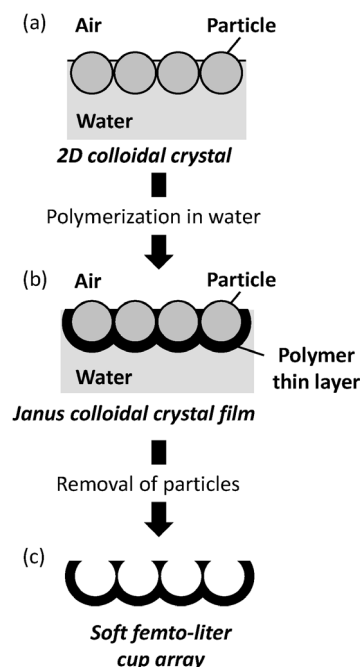


Figure 1. Schematic outline of the experimental procedure. a) 2D colloidal crystal adsorbed to the air–water interface. b) “soft” Janus colloidal crystal film adsorbed to the air–water interface following polymerization in aqueous solution to coat the water-exposed side of the 2D colloidal crystal. c) “soft” femtoliter cup array prepared by extraction of the particles from the Janus colloidal crystal film.

Poly(*N*-vinylpyrrolidone) (PNVP)-stabilized polystyrene (PS) latex particles were selected as model particles and were synthesized by dispersion polymerization of styrene (see Supporting Information).^[10] Scanning electron microscopy (SEM) studies indicated a number-average particle diameter of 2.50 μm and polydispersity of 1.01 (Supporting Information, Figure S1). PNVP was adsorbed to the PS particle surface as a colloidal stabilizer, and a colloidal stable latex dispersion was obtained. Unfortunately, X-ray photoelectron spectroscopy studies could not detect nitrogen atoms from PNVP on the PS particle surface. It was estimated by CHN elemental microanalysis that the PNVP loading was less than 2.4 wt % (the adsorbed amount of PNVP on the surface of the PS particles was less than 10 g m^{-2} , which was calculated assuming that all the PNVP existed on the particle surface). The 2D colloidal crystal was prepared as follows: a drop of a 2-propanol dispersion of PS particles, approximately 2 mm in diameter, at the end of a pipette was carefully brought into contact with the surface of an aqueous solution of pyrrole monomer (0.5 wt %). The particles spontaneously formed domains of 2D hexagonal crystals. The domain size of typical crystals in the monolayer (determined by optical microscopy)

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was in the range of 100–250 μm and the number of particles per crystal was between 40 and 2100; the average number was 330 particles (Supporting Information). The particles are held at the interface by capillary forces, which results in irreversible adsorption;^[11,12] for micrometer-sized particles capillary forces are much stronger than gravitational forces. The Gibbs energy required to remove the PS particle from the interface (ΔG) was estimated to be $8.07 \times 10^6 k_B T$ for a contact angle of 46° (see below) using Equation (1):^[13]

$$\Delta G = \gamma_{\text{aw}} \pi R^2 (1 - \cos \theta)^2 \quad (1)$$

Where, k_B is the Boltzmann constant and T is temperature, γ_{aw} is the surface tension of the air–water interface, R is the particle radius, and θ is a contact angle measured through the aqueous phase.

The system was left for two hours, so that the pyrrole monomer could swell the PS latex particles at the air–water interface. Then, an aqueous solution of FeCl_3 was added to the aqueous phase, and the polymerization was allowed to proceed for 24 hours at 25°C . The resulting black polypyrrole (PPy)-PS composite film was rinsed with pure water. The black color comes from the PPy, which is black because of the cation–radical nature and the extensive charge delocalization of PPy.^[14] In sunlight, the composite film showed vivid iridescence owing to light diffraction from the black PPy (Figure 2a inset). This phenomenon is the same as with black opals, where a silica colloidal crystal has a dark

particle uncoated (Figure 2b). The pyrrole only polymerized in the aqueous phase. Thus, the resulting PPy only coated the PS particle surface that was in contact with the aqueous phase. Even if some pyrrole exists on the air-exposed side of the PS particles, the FeCl_3 oxidant cannot come in contact with it, because its vapor pressure at room temperature is negligible.

The contact angle θ of the PS particle at the air–water interface (through water) was calculated to be $46 \pm 4^\circ$ using SEM images of the composite film observed from the air-phase exposed side and pristine PS particles (Figure 2b–d and Figure S4) using Equation (2)

$$\sin \theta = \frac{x}{R} \quad (2)$$

Where, x is the radius of the spherical cap of PS particles uncoated with PPy and R is the PS particle radius. To exclude the effects of PPy coating and determine the contact angle of pristine PS particles without any modification from PPy, the contact angle of a single PS particle was calculated from force-versus-position curves between the PS particle and a bubble, measured using colloidal probe atomic force microscopy (AFM; see Supporting Information).^[16] The average contact angle obtained by AFM was $41 \pm 5^\circ$, which is in agreement with the angle calculated from SEM images. This contact angle ($< 90^\circ$) indicates that the PS particles are relatively hydrophilic. In fact, the same PS particles can be used to stabilize aqueous bubbles and foams.^[10]

Contact angles of water drops on the Janus film from the air-phase and aqueous-phase exposed sides were measured to be 93° and 41° , respectively. This indicates that the film had hydrophilic and hydrophobic asymmetric character. When the Janus film was mixed with bromostyrene in water, the oil droplets were wrapped with the hydrophobic side facing the oil phase and the hydrophilic side facing the water phase (Figure 3a). When the film was transferred to the air phase, the film folded the hydrophilic sides together (Figure 3b). When it was transferred to the water phase, it folded in the opposite direction (Figure 3c). These folding-refolding cycles were reversible.

When the film was folded, the resulting double-layer showed Moiré patterns, which were observed by optical microscopy (Figure 3d and Supporting Information).^[17] Complex patterns were seen, with threefold symmetry over two length scales. The smaller-length scale is given by the hexagonal close-packed (hcp) structure of the PS particles. The longer-length scale is determined by the relative orientation of the two layers. Essentially identical Moiré patterns can be computer simulated by superimposing a digitized optical micrograph of an hcp PS latex monolayer onto the same image that has been rotated through angles of 7° , 9° , 13° , and 27° (Supporting Information). The formation of such Moiré patterns indicates a high degree of particle order within the Janus colloidal crystal films. Similar Moiré patterns were reported when two latex sheets comprised of arrays of micrometer-sized polymer particles were overlapped at different angles.^[10,18] However, such colloidal crystal films are more difficult to fabricate on a large scale than the air–water self-assembly method described herein. Colloidal

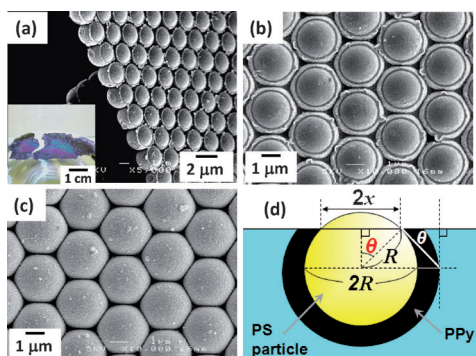


Figure 2. a–c) SEM images of a PPy-PS Janus colloidal crystal film and d) determination of the contact angle (through water) of the PS latex particle at the air–water interface using the SEM images. Inset of (a) shows the Janus colloidal crystal films floating on the water surface under sunlight. SEM images were recorded from the air-exposed (b) and water-exposed (c) sides of the film.

material in the background.^[15] PPy loading of the film was determined to be 10 wt % by thermogravimetric analysis. SEM images of the composite film revealed that the film had a colloidal-crystal structure with particle monolayer thickness (Figure 2a) and that PPy completely coated the PS particles that had been facing the aqueous phase (Figure 2c). The PPy overlayers have nanometer-sized surface roughness and the number-average thickness was measured to be 130 nm. The air-exposed side of the film showed incomplete coverage of the PS particles with PPy, leaving a spherical cap of each

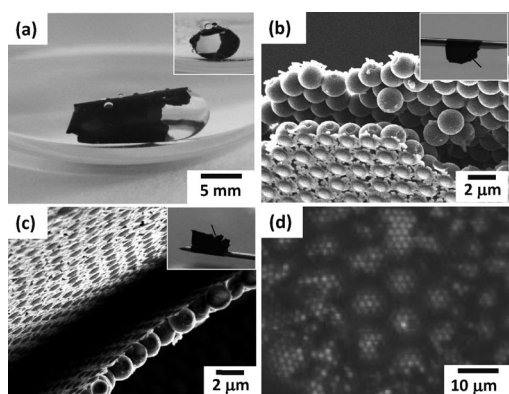


Figure 3. a) Optical photographs of a 4-bromostyrene oil droplet wrapped with the soft PPy-PS Janus colloidal crystal film in water (inset: front view). b,c) SEM images of folded PPy-PS Janus colloidal crystal film; the film was brought into b) air and c) water phases from the air-water interface. Insets show digital photographs of the self-folded films on a needle (diameter, 700 μm). d) Moiré patterns produced by the Janus colloidal crystal film bilayers as observed by optical microscopy. Note that particles (diameter, 2.50 μm) in the image had a similar diameter to that of the original PS particles.

crystals have generally been fabricated on flat, hard substrates and are difficult to form on curved substrates. The PPy-PS composite film, which was synthesized at the air-water interface, is soft and flexible, and can be transferred onto substrates with curvature. For example, the Janus composite film could be transferred to a stainless steel needle (diameter, 700 μm) to form a homogeneous coating (Figure 4).

It was shown that the PPy wall thickness can be controlled, between 60 and 420 nm, depending on PPy loading, keeping the 2D colloidal-crystal structure with

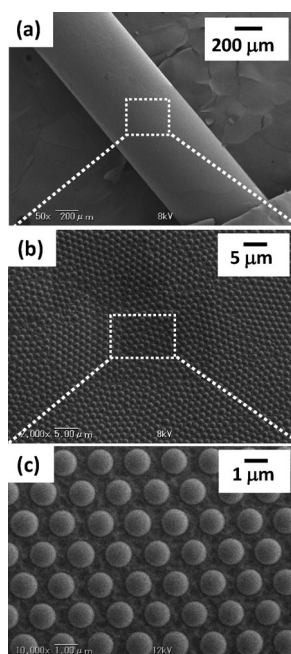


Figure 4. a–c) SEM images of a stainless steel needle (diameter, 700 μm) coated with the soft PPy-PS Janus colloidal crystal film at increasing magnification.

almost the same contact angles of PS particles at the air-water interface (43–48°; Supporting Information). Decreasing the pyrrole monomer and FeCl_3 oxidant concentrations led to a monotonic decrease in PPy loading. It was shown that a Janus film with an area of over $4 \times 10^2 \text{ cm}^2$ can be synthesized using the process described in this study. This method is general for the fabrication of Janus colloidal films, which in principle could be extended to include colloidal substrates other than polymer latexes, for example, inorganic oxides, silicates, and sulfides.

The PS particles could be removed using a suitable solvent. For example, we exposed PPy-PS composite films to tetrahydrofuran, which can dissolve PS but not PPy, arrays of micrometer-sized PPy cups were produced (Figure 5). This

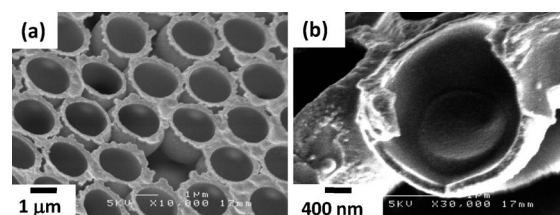


Figure 5. a,b) SEM images of PPy femtoliter cup array fabricated by extraction of the PS particles from the PPy-PS Janus colloidal crystal film using tetrahydrofuran. b) A magnification of the cross-section of the cup.

PPy cup array formed flexible films with a thickness reflecting the PS latex particle monolayer. It was also possible to coat substrates with curvature using the soft PPy cup-array film and to introduce the ordered cup structure on their surfaces (Supporting Information). Each cup has an average opening diameter of 1.80 μm and the volume of a single PPy cup was calculated to be 7.6 fL. It was possible to sieve solid particles using the femtoliter PPy cups and to adjust the number of the particles loaded into each cup by controlling the ratio of their dimensions; particles with diameters larger than the PPy cup opening could not enter the cups but particles with smaller diameters were loaded into the cup (Supporting Information). These PPy containers should be useful for femtoliter-scale chemistry.^[19]

Finally, the deposition of polymers onto 2D colloidal crystals other than PPy was also investigated (Supporting Information). Janus-type polyaniline (PANI)-PS 2D colloidal crystal films can be synthesized by aqueous oxidative polymerization of aniline using ammonium persulfate in the presence of a PS 2D colloidal crystal adsorbed to the air-water interface. A dark green PANI-PS composite film, which showed vivid iridescence under strong sunlight, was synthesized: the dark green color is due to PANI. The composite film was flexible and had Janus morphology; the air-exposed side of the film showed incomplete coverage of the PS particles with PANI, leaving a spherical cap of each particle uncoated, and PANI completely coated the PS particles on the aqueous surface. The contact angle θ of the PS particle at the air-water interface (through water) was calculated to be $47 \pm 4^\circ$ using SEM images, which corresponds well with the

angle calculated for the PPy-PS Janus film. A flexible PANI femtoliter cup array was also fabricated by extraction of PS particles from the Janus composite film.

In summary, a versatile strategy has been used to fabricate advanced materials (Janus-type 2D colloidal crystal films and femtoliter cup arrays), using an air–water interface as a place to introduce softness, asymmetry, and regularity. The Janus characteristic of the film results from the spontaneous adsorption of the colloidal particles at the air–water interface exposing faces both to air and water phases. The films are hydrophilic and hydrophobic on opposite sides and spontaneously fold in both air and aqueous phases. The Janus film and femtoliter cup-array film were soft and deformable and it was possible to coat curved substrates, to introduce patterned structures on their surfaces. The synthetic method presented in this study is scalable to produce bulk quantities of Janus colloidal crystal films and femtoliter cup arrays. Potential applications for these materials include novel soft-electronic and optical devices.^[20]

Experimental Section

Janus colloidal crystal film synthesis: A droplet of a 2-propanol dispersion of the PS latex particles (9.0 wt %) at the end of a pipette was carefully brought into contact with the surface of an aqueous solution of pyrrole monomer ($6.6 \times 10^{-3} \text{ m}^2$; 45 mL, 0.1–1.0 wt % based on aqueous media) until the whole water surface was covered. The pipette was held at an angle of approximately 30° to the water surface to reduce turbulence in the water. Under these conditions, regular 2D PS latex arrays were formed at the air–water interface, which showed the typical imperfections (packing faults, fault lines between crystallites) expected in a two-dimensional lattice. The coatings were made of hexagonal crystal domains of different orientation (see Figure S2). The system was left for 2 h so that the pyrrole monomer could swell the PS latex particles at the air–water interface. Then, FeCl_3 aqueous solution was added into the aqueous phase by syringe, and the polymerization was allowed to proceed for 24 h at 25°C . The Fe^{3+} /pyrrole molar ratio was 2.33 in order to ensure the production of PPy in high yield.^[21] The PPy-PS films were formed at the air–water interface (Figure S3) and were rinsed several times by placing the film with a special holder into fresh baths of pure water.

Colloidal probe atomic force microscopy: Colloidal probe measurements were carried out using a JPK Nanowizard atomic force microscope (JPK Instruments; Berlin, Germany). Single PS particles were fixed with two component epoxy glue (UHU end-fest 300, UHU GmbH; Bühl, Germany) to the end of a tipless silicon nitride AFM cantilever (type NP-OW, Veeco Instruments; Camarillo, CA, USA) with a nominal spring constant of 0.58 N m^{-1} with the help of a micromanipulator (Narishige MMO-203, Narishige Co. LTD; Tokyo, Japan) under an optical microscope (Zeiss Axiovert Vario, Carl Zeiss MicroImaging GmbH; Jena, Germany). Small air bubbles were placed at the bottom of a PS Petri dish filled with Milli-Q water using a syringe with a stainless steel needle. The Petri dish was placed on the inverted optical microscope of the AFM and the AFM was placed above the Petri dish. With the help of the inverted optical microscope, the AFM was aligned to the bubble position to place the colloid probe above the center of the air bubble. The stepper motor of the AFM was used to approach the colloid probe towards the bubble until first contact was achieved. From then the piezotranslators of the AFM were used to record cantilever deflection versus piezo position curves at a rate of one approach/retract cycle per second. When approaching the air bubble with the colloid probe, the colloid probe snaps into the air bubble upon contact. From this snap-in distance and

the particle diameter, the receding contact angle of the sphere can be calculated from Equation (3):

$$\cos \theta = \frac{R - D}{R} \quad (3)$$

where R is the particle radius and D is the jump-in distance, as shown in Figure S4b. A typical force versus piezo position curve is shown in Figure S5. Seven different colloid probes were used and for each contact angle and was determined from the average of at least 40 force curves.

Contact angle measurement of a water droplet on the Janus colloidal crystal film: Contact angles for water droplets (10 μL) placed on the Janus colloidal crystal films were determined 3 min after setting the water droplet using an Excimer SIMage02 apparatus at 25°C . Five separate droplets were investigated. Regarding the larger contact angle of water on the Janus colloidal crystal film surface (> 90 degrees) as compared with the PNVP-stabilized PS latex particles (46 degrees), we hypothesize that the surface of the PS particles may become hydrophobic to some extent after drying. This may be due to the diffusion of hydrophilic PNVP from the PS particle surface into the bulk. The contact angle of water on the Janus film was measured after approximately one week following Janus-film preparation, and it is possible that the PNVP on the surface of the PS latex particle diffused into the particles, which led to the hydrophobic surface. Kuroda and co-workers demonstrated that the contact angle of water on the polymer surface changed with time because of the diffusion of polar groups away from the surface into the polymer bulk.^[22]

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