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Simple Method for the Preparation of Colloidal Particle Monolayers at the Water/Alkane Interface

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Monolayers of monodisperse colloidal particles are formed by self-assembly. Such 2-D particle arrays are interesting objects for applications as lithographic masks, optical gratings, multilens arrays, antireflecting surface, synthetic membranes, data storage media, etc. Different techniques were proposed for the fabrication of such arrays. One approach uses monolayer film formation in a thin wetting film. In the simplest modification it consists of slow drying of the particle suspension prepared as a thin film on a solid or liquid substrate.^{1–7} More sophisticated modifications require special apparatus.^{8–10} Another approach relies on electrophoretic deposition of particles onto an electrode.¹¹ Both approaches have a drawback in the difficulty to control monolayer formation, because areas thicker than a monolayer can be formed. On the other hand, it is possible to build a monolayer on the liquid–air interface. Colloidal particles apparently can be trapped at the liquid surface as a result of the electrostatic and surface tension forces.^{12–15} However, application of the Langmuir–Blodgett (LB) technique to colloidal particles led to sub-monolayers with a coverage not more than 80%.^{16,17} Only recently Tredgold and co-workers¹⁸ reported on the successful Langmuir–Schaefer transfer of monolayers of silica particles modified with 3-aminopropyl groups. However, the properties of these arrays were not reported in detail. Kondo et al.¹⁹ were able to fabricate close packed 2-D arrays of silica particles

transferred from benzene/air interface by a simple technique without using a LB trough. However, this requires an additional chemical step of silica particle modification by alkoxylation. Only particles modified with dodecyl chains (thus highly hydrophobic) formed ordered close packed monolayers. The authors¹⁹ believe that the monolayer formation involves a two-stage process with particles laterally moving on the solid substrate to form finally close packed array. Recently Aveyard et al.²⁰ investigated the monolayer behavior of polystyrene (PS) particles at the water/octane interface and found a formation of highly ordered arrays of large 1.5 and 2.6 μm particles. The particles were highly repulsive in contrast to the behavior at the air/water interface. In this work no attempt to the transfer of particles onto a solid substrate was reported. Thus it seems that despite many years of studies of the behavior and aggregation of colloidal particles at the water/air interface^{12–23} there is still a lack of data on the transfer of the monolayer onto the solid substrates.

The recent results^{18,20} led us to a new very simple and fast method of the fabrication of close packed arrays of large latex and silica particles. Large particles have also the advantage to be easily imaged by optical microscopy. We used monodisperse 0.74 and 1.2 μm polystyrene (PS) particles (obtained according to ref 24 by an emulsifier-free, aqueous radical polymerization), 0.94 μm polystyrene-2-hydroxyethyl methacrylate (PS–HEMA) particles, 1.2 and 1.4 μm polystyrene-2,3-epoxypropyl methacrylate (PS–EPMA) core–shell particles (PS core particles were equipped with a hydrophilic shell according to ref 25), 2.5 μm sterically stabilized tentacle PS particles (obtained according to ref 26 by nonaqueous dispersion polymerization, containing poly(vinylpyrrolidone) shell), and 0.8 and 1.7 μm plain silica particles (Micromode GmbH, Rostock, monodispersity of large particles was improved by several sedimentation steps).

Monolayers of particles were prepared by spreading of the EtOH suspension (ca. 5% w/w) of the particles onto the interface between water and a thin layer of hexane or heptane in a Petri dish until the water surface is totally covered with the monolayer. The substrate (precleaned glass slide) was preliminary placed in the bottom of the dish. Then either the substrate was lifted up through the monolayer with a tweezer or the monolayer was lowered onto the substrate by decreasing the water level (taking water with pipet) (Scheme 1). Another possibility was to use a separation funnel (Figure 1) instead of a Petri dish and remove slowly the water similar to conical trough, a technique described in refs 27 and 28. In this way the wall of the funnel (or the surface of any shape) can be also covered with monolayer. Large close packed monolayers of about 2 cm^2 could be easily and quickly obtained by this

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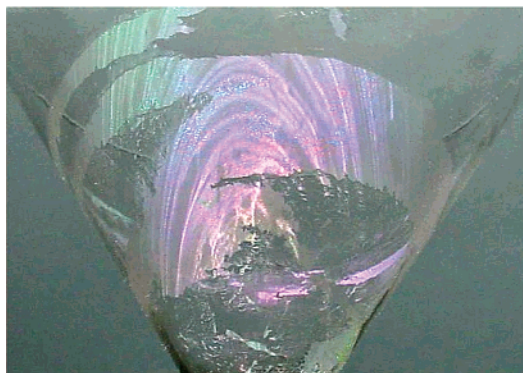
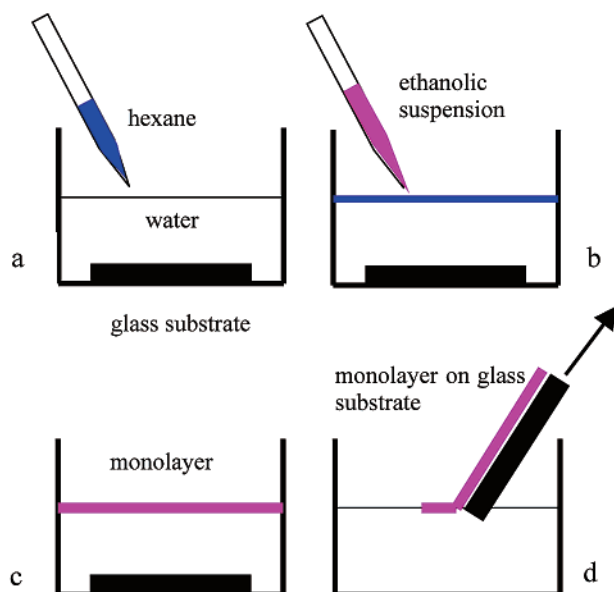


Figure 1. Photograph of the monolayer film of $1.4\ \mu\text{m}$ PS-EPMA core-shell latex particles on the separatory funnel upon illumination with white light.

Scheme 1. Schematic Description of the Fabrication of Particle Monolayer by Transfer from the Water-Hexane Interface: (a, b) Spread of Particle from EtOH Dispersion on the Water-Alkane Interface; (c) Formation of the Floating Hexagonal Arrays of Particles; (d) Transfer of Particle onto Solid Substrate



technique. The layer exhibits diffraction colors upon illumination with white light (Figure 1). Individual particles and the monolayer structure could be imaged by optical microscopy (Figures 2 and 3). Close packed hexagonal arrays (with point defect and dislocations) are clearly seen. The ordered arrays are large enough for hexagonal diffraction to be observed by diffraction microscopy with a Bertrand lens^{29,30} (Figures 2 and 3, insert). In this way, well-ordered monolayers were obtained with 1.2 and $1.4\ \mu\text{m}$ core-shell particles and silica particles. This preparation method also succeeded for a $1.2\ \mu\text{m}$ core-shell latex which was additionally modified with a coumarin dye on the surface. This results in particles and arrays, which are fluorescent and can be photochemically modified upon irradiation. For other particles the monolayer quality was inferior (Figure 3a). These monolayers were similar to arrays obtained by the Langmuir-Schaefer technique using $1.4\ \mu\text{m}$ core-shell particles (Figure 3b).

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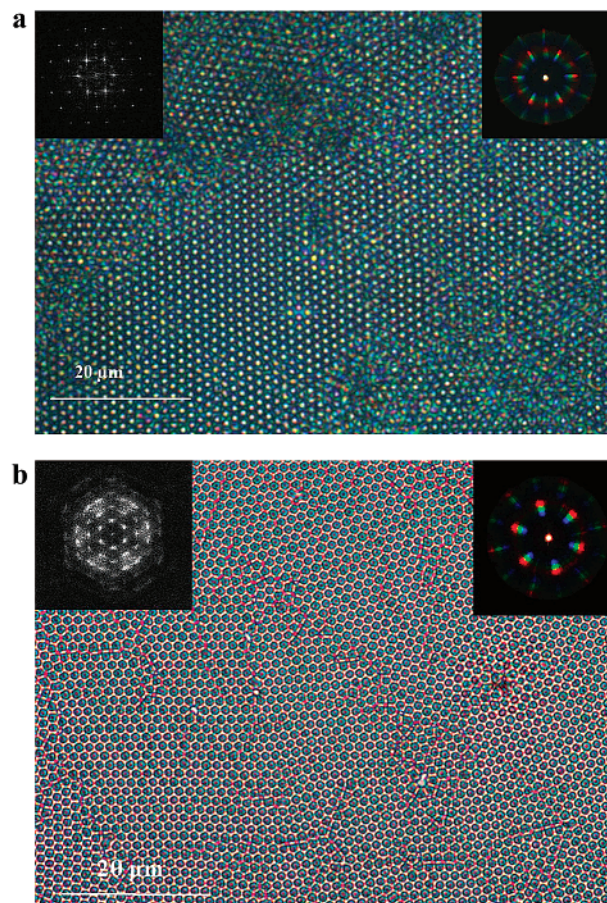


Figure 2. Microscopic image (objective $100\times$) of a monolayer of PS-EPMA ($1.4\ \mu\text{m}$) (a) and silica ($1.7\ \mu\text{m}$) (b) particles transferred from the water/hexane interface. Corresponding diffraction images with Bertrand lens (right insert) and 2D-FFT transformation (left insert, 512×512 pixels) are shown.

For comparison of the monolayers obtained, the number of particles in ordered domains was estimated. While in good samples ($1.4\ \mu\text{m}$ core-shell latex and $1.7\ \mu\text{m}$ silica) the number of particles in single crystalline domains was more than 100 and for $1.2\ \mu\text{m}$ PS-EPMA modified with coumarin dye at least 100, for other particles and for $1.4\ \mu\text{m}$ core-shell PS monolayers obtained by the Langmuir-Schaefer technique this number was at the level of 10–30 or sometimes even lower. The array quality could be also estimated by 2D-FFT (fast Fourier transform) of the images from optical microscopy³⁰ (Figures 2 and 3, insert). The FFT image shows a distinct hexagonal pattern, if the size of the single crystalline domain in the array is larger than the square area of the transformation.

We followed the formation of the particle arrays on the water/alkane interface by optical microscopy and proved that the hexagonal ordered structure is quickly formed already on the interface. After that, the preformed arrays are transferred onto the solid substrate. The changes in the domain direction are formed already on the water/alkane interface as the monolayer islands are swimming at the interface followed by sticking together with increasing surface concentration. Hexagonal ordered islands are moving on the water surface until they meet another island. Finally, when the concentration of particles on the water surface is sufficient, a full monolayer is formed that can be easily transferred onto the solid support. Tentatively, the array quality at the water/alkane interface is superior due to stronger repulsive interactions.²⁰

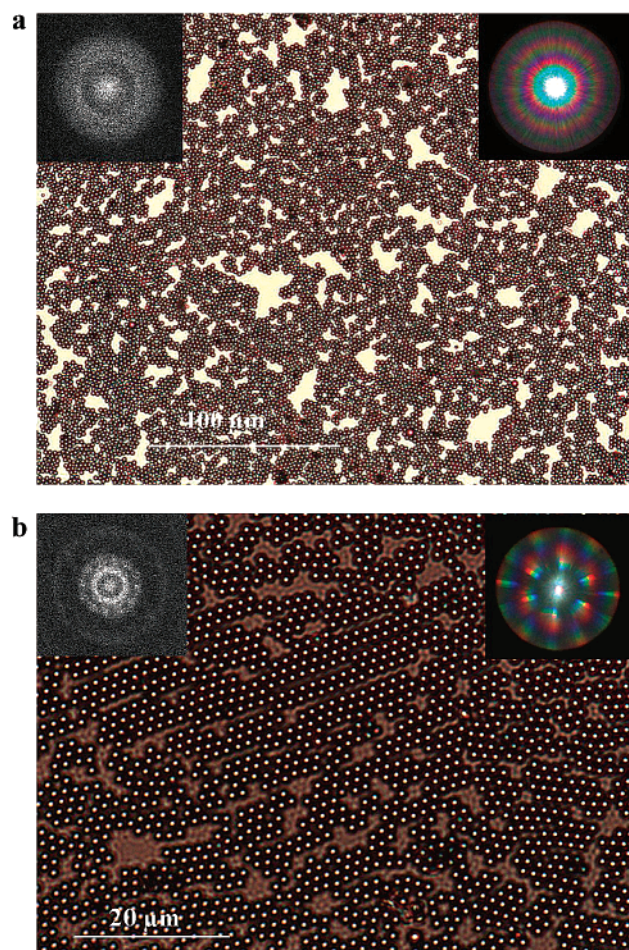


Figure 3. (a) Microscopic image (objective 20 \times) of a monolayer of 2.4 μm sterically stabilized PS particles. (b) Microscopic image (objective 100 \times) of a monolayer of 1.4 μm PS-EPMA core-shell particles transferred by the Langmuir-Schaefer technique. Corresponding diffraction images with Bertrand lens (right insert) and 2D-FFT transformation (left insert, 512 \times 512 pixels) are shown.

Also it seems that both particle size and the balance of hydrophilic/hydrophobic properties play a crucial role

resulting in the different monolayer quality. Control experiments at the water/air interface as well as the Langmuir-Schaefer transfer method (Figure 3b) for 1.4 μm particles resulted only in a island-type structure, confirming the important role of the alkane top layer.

Preliminary studies showed that such nanostructures could be transferred not only onto hydrophilized glass surfaces but also to polymer films. This could be interesting for the application of colloidal particles in nanolithography.

Particle monolayers on the water interface can be additionally stabilized by photochemical polymerization and in such a way even free-standing monolayers can be easily accessible. In such a simple experiment UV-curable glue (Norland NOA 61) was introduced in the hexane top layer. Upon illumination with UV light the particle monolayer was frozen on the water surface and a free-standing flexible monolayer film was picked up. Microscopic investigation of either photopolymerized monolayers on the water surface or free-standing film exhibited similar hexagonal close packed particle organization.

In summary, a very simple and fast technique was developed to organize hexagonally ordered monolayers of hydrophilic micrometer size PS and silica particles at a water/alkane interfaces and to transfer them onto solid substrates. These monolayers showed good diffraction properties as observed by optical microscopy with a Bertrand lens. This technique can find application in lithography using colloidal particle arrays or in membrane fabrication of narrow pore size (particularly photopolymerized free-standing monolayers). Further modifications and improvements could be possibly achieved by varying the organic phase and the composition of the water phase (electrolytes, surfactants).

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