Size-Discriminative Self-Assembly of Nanospheres in Evaporating Drops

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Evaporation of liquid drops containing nanospheres resulted in circular deposition patterns. The circularity of the patterns depended on the uniformity of the surface tension on the substrate. By employing binary suspensions, containing two differently sized nanospheres, it was possible to modulate the fine structure of such rings. Slow evaporation on mirror-polished substrates resulted in well-ordered distributions, where larger particles self-assembled in dense hexagonal packages, forming apparently an external ring, deposited around the massive inner ring. Deposition started at the air/liquid/solid-contact line. Results could inspire principles for the fabrication of optical devices and may be fruitfully used to design biomaterials with cell-selective properties. A simple model is employed to predict the radial arrangement of nanospheres in rings. Deviations from a standard order (predicted by the model) may be useful to detect biologically active nanoparticles.

Perfectly symmetrical self-organized rings can be found on various scales. Massive rings with diameters up to two meters, formed at the ground by stones the size of a walnut, have been observed in polar regions.[1] Millimeter-sized rings have been observed to form from droplets of a nanosuspension evaporating on substrates.[2] Microscale rings have formed by the evaporation of droplets of a nanoemulsion deposited on surfaces via inkjet printing methods.[3,4] The physical mechanism responsible for the formation of rings has been analyzed extensively.[5] Except for some aesthetic aspects and a theoretical interest in the mechanism of their formation, the rings did not attract much attention. However, the situation has recently changed with the realization that such regular structures, representing virtually adjustable molds, could be instrumental for the design of cell-integrative biomimicry patterns on biomaterial surfaces[2] and could inspire practicable strategies for the encapsulation of atmospheric ozone killer condensates.[6] Circular molds represent ideal frames for the lithographic production of microlens array systems mimicking natural biosystems.[7] Several groups have reported on rings formed from nanoparticle suspensions.[8,9] Ring formation has been described for various nanoparticles: silver, copper, cobalt, cadmium sulfide, barium ferrite, and gold. The mechanism of formation has been explained in terms of the interaction between wetting properties, capillary forces, surface tension, and evaporation-driven convective flows resulting from temperature gradients.

As in various similar situations, possible nanotechnological developments have stimulated a reconsideration of previously described macroscopic physical mechanisms. For example, a closer examination of the stone rings revealed that the material in the area enclosed by the rings had a finer grain structure than that constituting the body of the rings—a phase separation phenomenon. The mass of the stones excludes gravity as a possible substantial factor forming the natural ring patterns. However, for nanoparticles suspended in liquid drops, gravity is likely to considerably affect both dynamics (rate of sedimentation) and pattern formation in the rings. To analyze the impact of gravity on pattern formation, we investigated mass-discriminative separation processes in millimeter-scale rings, formed by the evaporation of drops of suspensions containing differently sized nanospheres. To the best of our knowledge, the known ring patterns induced by drops evaporating on solid surfaces have been realized by the use of nanosuspensions based on particles having solely one size. In this way, the effect of gravitational force on particle deposition has never been observed. Extension of the existing models to suspensions containing differently sized nanospheres requires the implementation of the two principal evaporation routes (lateral and

Figure 1. Light microscopy image of a ring formed by slow evaporation of a drop of an aqueous suspension containing 60 nm nanospheres on mirror quality titanium disk. Deviation from circularity (cf. Figure 2) indicates nonuniform contamination of the titanium surface. Ring diameter ∼ 4.2 mm.

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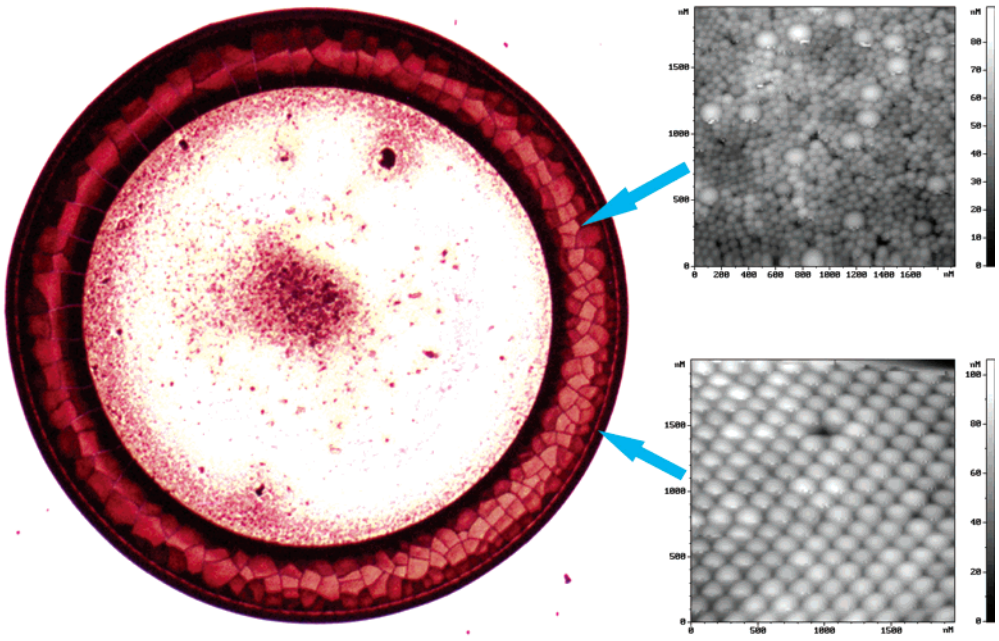

Figure 2. (left) Light microscopy image of a perfect ring formed by slow evaporation of a drop of an aqueous suspension of a mix of 60 and 200 nm nanospheres on mirror quality titanium disk. (right) Representative AFM images of the topography of a similarly composed mixed phase ring formed under identical conditions on mica: predominantly 60 nm nanospheres on the top, densely packed highly ordered crystalline structure formed by 200 nm nanospheres at the periphery of the ring. Mica has been used to obtain the best possible AFM−images. Ring diameter ~5 mm.

vertical), and their net action on particle sedimentation and pattern formation. An analysis of the parameters controlling these routes could provide relevant data for various deposition processes, including the self-organization of biomolecules (varying in size by several orders of magnitude) confined to the interior of hydrophobic drops, partially or completely surrounded by an aqueous environment. Prior to surface contact, nanoparticles start competing for space. Here, gravitational sedimentation is accompanied by van der Waals interaction energies. These energies, discriminating between chemically different nanoparticles, and affecting their deposition in the near-field of the substrate, may be implemented into the existing concepts. For spherical particles interacting with a surface, the interaction energy has the simple form $W = -AR/6D$, where A is the Hamaker constant, R the radius of the particle, and D the distance between particle and surface. Clearly, any shift from an expected deposition pattern could represent valuable information, and may serve as an indicator for the presence of additional components coating the nanoparticles. Particularly adhesive films could promote the attachment of nanoparticles to another and/or to substrates. The prototype for such a coating could be the slime secreted by nanoscale biosystems (e.g., living nanovesicles).[10] Deviations from an expected size-dependent standard distribution of the particles in rings could be of practical use to predict the presence of materials of biological origin in drops with a defined composition of nanospheres. For substrates with a uniform surface roughness, deviation of the ring shape from circularity is a clear indicator for an inhomogeneity in surface tension (Figure 1). This could stem from surface active materials, discontinuously distributed on the substrate. In this way, surface contaminations could be qualitatively analyzed − quick, simple and at a low cost.

In this letter we report on ring and nanoscale structuring by slow evaporation of aqueous droplets containing polystyrene nanoparticles of two different sizes. When 10 μL drops of a monodisperse suspension with 60 nm polystyrene nanospheres were placed on mirror-polished titanium disks (total surface roughness less than 4 nm)[11] and allowed to evaporate slowly

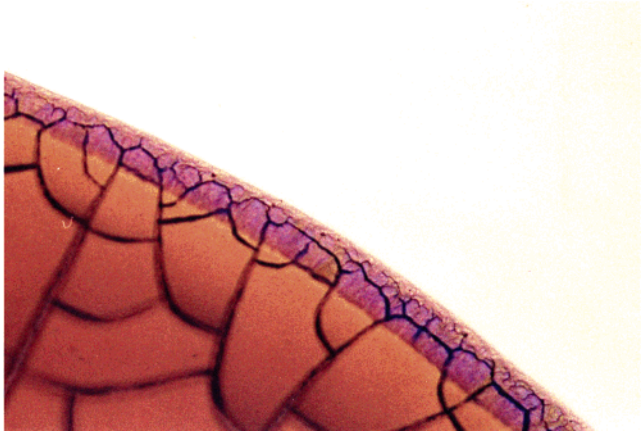

Figure 3. Representative bluish margin at the periphery of the ring reveals the highly ordered crystalline phase consisting of 200 nm nanospheres.

in air-sealed Petri dishes (Ø 35 mm), perfect rings were formed.[2] In droplets containing equal volumes of 60 and 200 nm polystyrene nanospheres, the central field within the rings showed a clear tendency for an accumulation of some particles (Figure 2). Optical and atomic force microscopy (AFM)-inspection of the thin film enclosed by the rings revealed a significant number of larger particles, assembled in the central ring zone. The inspection of rings formed by the differently sized nanospheres by optical microscopy revealed in all cases a bluish margin at the periphery of the ring, indicating an ordered crystalline phase (Figure 3). The fine structure of the ring was evaluated by AFM. It was surprisingly found that the bluish rim was practically composed of 200 nm particles only (Figure 2), while the field around the ring-apex contained a clear majority of 60 nm nanoparticles (Figure 2). Furthermore, we found that the 200 nm nanoparticles forming the bluish rim self-assembled in a hexagonal, two-dimensional order. Similar phenomena have been observed on mica surfaces, indicating that here, particle-size related structuring and distribution did not depend on the material of the substrate employed.

The images presented permit visualizing the interplay between the major factors determining the transport of suspended material: (**1**) depletion in surface tension at the air/solid/liquid interface (pulling nanospheres along with water molecules escaping at the surface tension sink at the drop margins), (**2**) vertical temperature gradient (driving nanospheres to ascend toward the drop apex), and (**3**) gravity (causing sedimentation and discriminating between particles differing in mass). Once the larger particles are pinned down at the outermost ring margins, they serve as starting line for the crystalline assembly. The trajectory of a suspended nanosphere, starting at the bottom of a droplet, will eventually end on top of the ring. For a convective flow with a vertical temperature distribution and a certain ring altitude, various larger nanospheres that have landed on the ring crest, will subsequently roll down from the curved ring surface dominated by 60 nm nanospheres, in accordance with observation. Reducing rings to the dimension of living cells, and modifying exclusively the topography of the film enclosed by the ring, and/or of the outmost ring margins, is of particular interest for the realization of nonspecifically operating biomimicry architectures on scaffolds[2] − cell-integrative (facilitating cell attachment) and cell-selective (inhibiting cell attachment). Such multifunctional structures could be achieved by adjusting the drop size to the dimension of cells, and a proper choice of differently sized nanoparticles. Interestingly, the same arguments apply for the production of microlenses, where rings allow to precisely control the lens radius. In binary suspensions, larger nanospheres are more effective in creating rings of a circumference matching the initial contact line between drop and substrate than are smaller beads, simply due to quicker sedimentation and stronger adhesion to the substrate. The hexagonal packing at the periphery of such rings appears to be associated with a special advantage, as indicated by three-dimensional quantum dot lattices formed by a bimodal size distribution of nanocrystals, showing new optical properties compared to a unimodal particle distribution.[12] It could be expected that two-dimensional regular arrays of such rings will exhibit unique light-collective properties.

An understanding of the complex interplay of the parameters influencing both the micro and the nanostructure in self-organized pattern formation processes may be also important in novel tissue engineering applications, where droplets of suspensions containing populations of living cells and biomolecules are deposited on scaffolds via ink-jet printing methods.[13] Final clarification of the effect of the individual forces experienced by nanospheres in evaporating suspensions could be expected from experiments carried out in microgravity.

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