

Phase Separation gives Rise to Nanoparticle Ring Formation

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We report on the formation of self-assembled rings of CoPt₃ nanoparticles in ultrathin polymer films (ring diameter about 1 μm , particle diameter 6 nm). The polymer thin film was formed by wetting a polymer solution on the surface of water. The process of self-assembling turns out to result from phase separation of the binary polymer solution film used, the subsequent dewetting of the top layer, and its decomposition into droplets on the surface of the bottom layer.

Key words: Self-Assembly; Nanoparticles; Phase Separation; Wetting; Dewetting; Polymer Thin Film.

1. Introduction

Nanoparticle assemblies have generated increasing interest in materials science during the last years. Their collective physical properties, which both qualitatively and quantitatively differ from the ones of bulk materials, depend on particle size, spacing, and the order of structure [1,2]. Various methods have been developed for directing the self-assembly of nanoparticles into ordered aggregates. It has been recently demonstrated that Co nanoparticles can self-assemble in two-dimensional (2D) arrays following a long-range order [3]. There, magnetic metal particles experience a strong van der Waals attraction which, combined with their magnetic dipole interactions, makes stabilizing these systems a rather challenging task. Tripp et al. [4] have shown that Co nanoparticles can self-organize into bracelet-like rings which can be formed by two different mechanisms: dipole-directed self-assembly and evaporation-driven hole formation in viscous wetting layers. One-dimensional arrangements of metal nanoparticles are generated by self-assembly processes that take place at the phase boundary between water and dichloromethane [5].

In this work, we present experimental results on the interconnection between phase separation in a multi-component polymer mixture and the formation of self-assembled rings of CoPt₃ particles in ultrathin polymer films (ring diameter about 1 μm , particle diameter 6 nm).

2. Experimental

The polymer thin film was prepared during the wetting process of a polymer solution on a water surface [6, 7]. The polymer system being considered is a blend (B) that contains 50 weight-% of a 1 % nitrocellulose solution (NC) in amyl acetate and 50 % of a CoPt₃ particle solution in hexane with hexadecylamine (HDA) as stabilizing agent. The concentration of the particle solution (including hexadecylamine) was 24 mg/ml. CoPt₃ particles with a diameter of 6 nm were prepared via the simultaneous reduction of Pt(acac)₂ and thermal decomposition of Co₂(CO)₈ in the presence of 1-adamantanecarboxylic acid (ACA) and hexadecylamine both functioning as stabilizing and size-regulating agents [8]. The surface tension coefficient of the blend has been determined to $\gamma_{B/A}(20\text{ }^{\circ}\text{C}) = 22.8\text{ mN/m}$. As for the other liquid surface on which we have stacked the polymer thin film, we used distilled water (W) exhibiting a surface tension coefficient of $\gamma_{W/A}(20\text{ }^{\circ}\text{C}) = 72.5\text{ mN/m}$. The above quantities $\gamma_{B/A}$ and $\gamma_{W/A}$ designate the surface tension at the boundaries between blend and air (B/A) and between water and air (W/A), respectively.

Wetting of the blend solution on the water surface is achieved [9] when the wetting coefficient $S_{B/W} = \gamma_{W/A} - \gamma_{B/A} - \gamma_{B/W}$, is $S_{B/W} > 0$. Here, $\gamma_{B/W}$ gives the surface tension at the interface between the blend solution and water. In our case, total wetting of the fluid B drop on the water surface is attained, because we have $S_{B/W} = 25.3\text{ mN/m}$ with $\gamma_{W/A} = 72.5\text{ mN/m}$, $\gamma_{B/A} =$

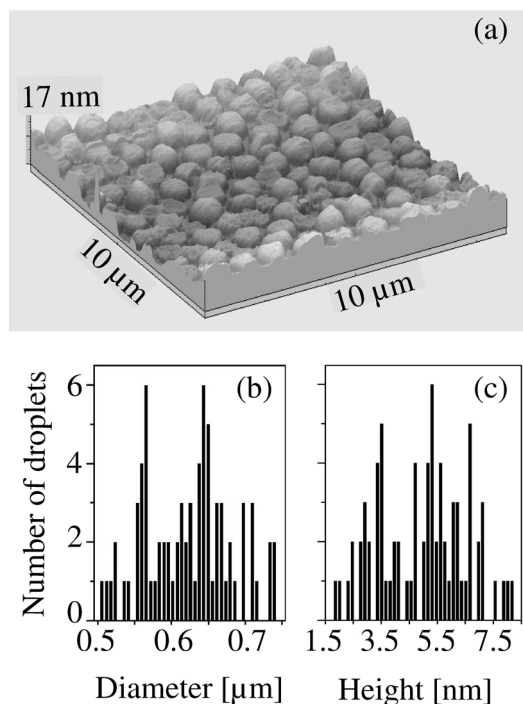


Fig. 1. AFM image of smallest-size hexadecylamine droplets on a cellulose film. The mean size of the droplets is given by the diameter $D_d = 650$ nm and the height $h_d = 5.0$ nm. (a) Three-dimensional representation; (b) and (c) are histograms of the diameter and height distribution of the droplets, respectively.

22.8 mN/m, and $\gamma_{B/W} = 24.4$ mN/m. The values of the surface tension were determined by the help of a stalagmometer. This setup consists of a capillary tube the polymer solution flows through, which enables the counting of the number of droplets, measuring their volume and weight, and, thus, the derivation of the surface tension (via calibration with distilled water). Since the volume of the spread drop was $3 \mu\text{l}$, the total thickness of the resulting spread fluid layer (with a diameter of 86 mm) can be estimated to about 600 nm.

The topography of the solid polymer thin films was analyzed by atomic force microscopy (AFM, model Burleigh Vista 100); these experiments were performed in the AC mode where a vibrating tip is being scanned over the surface. The arrangement of the CoPt_3 particle rings was monitored by transmission electron microscopy (TEM, model Zeiss EM 902).

3. Results and Discussion

After evaporation of the solvent from the blend solution film, asea-island-like phase separated structure

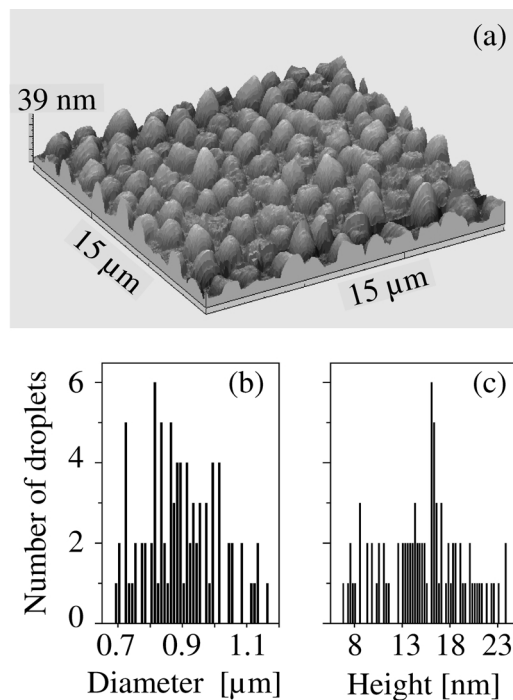


Fig. 2. AFM image of the middle-size hexadecylamine droplets on a cellulose film. The mean size of the droplets is given by the diameter $D_d = 950$ nm and the height $h_d = 14.9$ nm. (a) Three-dimensional representation; (b) and (c) are histograms of the diameter and height distribution of the droplets, respectively.

of hexadecylamine (furtheron called HDA droplets) on the cellulose thin film could be observed. The size distribution of the HDA droplets depends on the location chosen along the radius on the spreading solid film. Also the height h_d of the isolated droplets varied from 5 to 23.5 nm along the radius when it changed from 0 (center of the spreading layer) to 20 mm. The corresponding diameter D_d of the droplets varied from 0.6 to 1.5 μm .

Figures 1 (a), 2 (a), and 3 (a) show typical AFM images of the structure of the HDA droplets located on the surface of the cellulose film, differing in the average droplet height h_d of 5.0 nm, 14.9 nm, and 23.5 nm, respectively. The corresponding values of the average diameter D_d are 650 nm, 950 nm, and 1497 nm, respectively. It should be noted that the droplets in all samples investigated are aligned with some curvature, extending over a length of a few tens of μm . The droplets of small size can be connected with or separated from each other, see Figure 1 (a). The distance between the droplets increases with the size of the droplets, so that

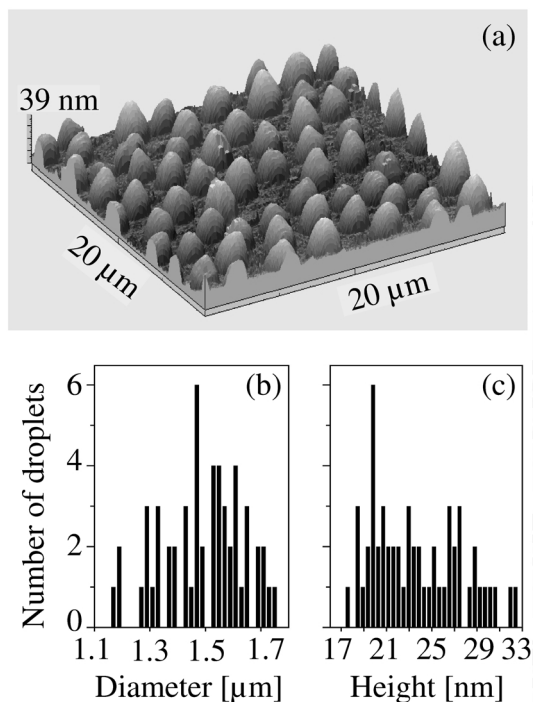


Fig. 3. AFM image of the largest-size hexadecylamine droplets on a cellulose film. The mean size of the droplets is given by the diameter $D_d = 1497$ nm and the height $h_d = 23.5$ nm. (a) Three-dimensional representation; (b) and (c) are histograms of the diameter and height distribution of the droplets, respectively.

the large droplets became more isolated, see Figure 3 (a). For small droplets (Fig. 1 (a)), we recognize that some of them have an M-like profile, but the large droplets were always round and convex to some extent (Fig. 3 (a)). The uniformity of the droplet distribution increases with the droplet size, as clearly illustrated in Figs. 1 (b), 2 (b), and 3 (b). The small droplets are well characterized by the two maxima in the histogram of the diameter distribution. Apparently, the pronounced first maximum in Fig. 1 (b) diminishes in Fig. 2 (b) and, finally, almost disappears in Figure 3 (b). A similar behavior can be observed in the histogram of the height distribution displayed in Figs. 1 (c), 2 (c), and 3 (c). The latter indicates that the lateral growth of the droplet size is approximately proportional to its vertical growth. It turns out that the distribution of the droplet diameter shown in Fig. 3 (b) is comparatively narrow, centered around the mean value $D_d = 1497$ nm with a standard deviation of ± 191 nm. This means that about 70 % of all values of the droplet diameter are confined to the interval (1497 ± 191) nm. The error

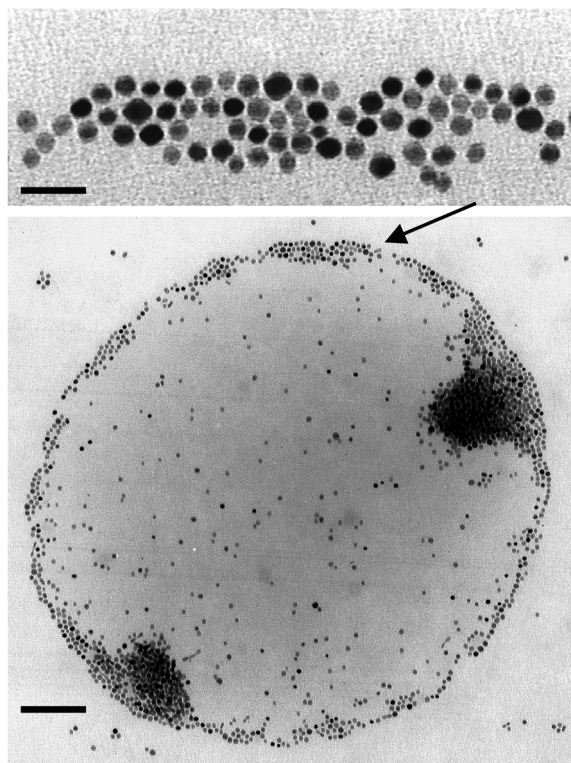


Fig. 4. TEM image of a CoPt_3 particle ring formed at the edge of the hexadecylamine droplet. The detailed structure is magnified above. Scale bar 108 nm (inset 20 nm).

range of the mean value of D_d is estimated to ± 26 nm. The corresponding distribution of the droplet height in Fig. 3 (c) unveils a mean value $h_d = (23.5 \pm 0.6)$ nm with a standard deviation of ± 4.3 nm.

As we learn from our TEM investigations on the droplet structure, the CoPt_3 particles are obviously self-assemble into a ring pattern located at the droplet edges. Figure 4 shows a TEM image of a single HDA droplet with a diameter of $D_d \approx 820$ nm, emphasizing the corresponding ring of particles. It can be clearly recognized that the particles are hexagonally packed and the distance between individual particles in the ring is roughly constant.

We have found that the cellulose layer extends from the substrate surface to ambient air, i. e., the substrate is completely covered by a cellulose film (with thickness 3–4 nm). The HDA droplets are well situated on the cellulose surface and do not have direct contact to the substrate surface. The depth of the void that remained in the cellulose film after removal of the HDA droplets (by immersing into hexane) was about 0.5 –

1.0 nm, indicating that the thickness of the cellulose film under the voids amounts to at least 3 nm. Following this experimental result, we propose that the initial thin solution layer is transformed into a bilayer structure which consists of a hexadecylamine-rich (HDA-rich) phase at the solution-air interface with thickness ≤ 300 nm and a cellulose-rich (NC-rich) phase at the solution-water interface with thickness ≤ 300 nm. One reason for the above process is that a solution component with lower surface free energy enriches at the surface region, in order to minimize the free energy at the interface between air and the polymer solution [10–14]. From our measured data, we extract a surface tension of 21.8 mN/m for a 1 % solution of cellulose in a common binary solvent (50 % amyl acetate, 50 % hexane). The corresponding value for a 0.5 % solution of hexadecylamine in a similar solvent amounts to 21.2 mN/m, indicating that the HDA-rich phase has a lower surface free energy than the NC-rich phase.

The subsequent process, which comes into play by the solvent evaporation, is the dewetting of the HDA-rich layer on the NC-rich layer. There exists a critical thickness, below which the HDA-rich layer is unstable and thermal fluctuations of the layer thickness take place [15, 16]. Hence, the HDA-rich layer decomposes into droplets. The drying process of a droplet of the HDA-rich phase with CoPt₃ particles gives rise to a motion of the contact line (interface between air, liquid, and substrate) to the interior. We assume that those particles that are located at the contact line follow its shrinking procedure and, therefore, are assembled in a

ring-like structure under the action of capillary forces. On the other hand, as the contact line is pinned, an outward flow of the common solvent develops. This happens because the solvent that via evaporation is removed from the edge of the droplet must be replenished by a flow of the solvent from the interior [17–19]. This flow can transfer up to 100 % of the solute to the contact line [19]. In future work we intend to look at the correlation between the number of particles which are assembled at the contact line during its motion and the number of those particles which move to the contact line with the solvent flow.

4. Conclusion

We have experimentally demonstrated that self-assembly of rings of CoPt₃ nanoparticles in ultrathin polymer films derives from phase separation of a binary polymer solution on top of a water surface. The latter process leads to the formation of a bilayer structure which consists of a hexadecylamine-rich layer at the solution-air interface and a cellulose-rich layer at the solution-water interface. The subsequent dewetting of the top layer on the surface of the bottom film enforces its decomposition into a hexadecylamine droplet pattern, at the edge of which the CoPt₃ particle rings develop.

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