Advanced Powder Technology 24 (2013) 897–907

Contents lists available at SciVerse ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Review paper

Particulate pattern formation and its morphology control by convective self-assembly

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ARTICLE INFO

Article history:
Received 22 March 2013
Received in revised form 3 May 2013
Accepted 3 June 2013
Available online 19 June 2013

Keywords:
Self-assembly
Patterned structure
Template-free
Drying
Particulate film
Bottom-up approach
Convection

ABSTRACT

Bottom-up self-organization approaches are promising for fabricating higher-order patterned surfaces composed of colloidal particles. The first example among the patterns that have been extensively studied would be stripes; however, the formation of stripe patterns has so far been confined to partially or fully hydrophobic surfaces. By contrast, we have succeeded in preparing well-defined stripe patterns even on strongly hydrophilic substrates via a convective self-assembly technique. By using this technique, a stripe pattern was produced simply by suspending a substrate in a dilute suspension, without any complicated procedure; the stripes spontaneously aligned parallel to the contact line. Driven by this finding, we further investigate this self-assembly process, and find out that the convective self-assembly is quite promising as a template-free pattern formation technique. In the present paper, we first overview the convective self-assembly technique which is originally developed for uniform film formation, and then present our recent results on the pattern formation of colloidal particles through the convective self-assembly. This technique can produce various patterns including stripes, cluster arrays, and grids in response to macroscopic experimental parameters such as particle concentration and temperature.

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1. Introduction

Significant progress has recently been made in techniques of surface patterning over large areas because micro-, meso-, and nanostructured surfaces exhibit anomalous properties due to enhanced interfacial effects [1–3]. Colloidal particles are fundamental building elements for fabricating patterned structures on a substrate including stripes, rings, grids, and dot-arrays, which can find potential applications such as controlled cell growth platform [4], transparent conductive electrodes [5,6], and plasmonic sensing materials [7]. The fabrication of complex particulate patterns in a precisely controlled manner has been achieved by top-down lithography techniques, e.g., photolithography, laser interference lithography, and electron-beam lithography. Although these top-down approaches are quite effective, the use of bottom-up self-assembly processes becomes necessary to complement them as the required structure sizes become of the order of nanometers. The advantages of self-assembly techniques are its simplicity, versatility, cost-effectiveness, and compatibility with heterogeneous

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0921-8831/$ - see front matter
http://dx.doi.org/10.1016/j.apt.2013.06.001

integration processes [8–10]. Among various techniques so far reported, a widely-used one is template-directed colloidal self-assembly. In this approach, a suspension droplet is allowed to evaporate on a topologically grooved substrate which acts as a template to guide and arrange the particles into the desired pattern with the aid of the convection that brings the particles to the drying front [11–13]. Instead of the topological modification, the use of chemically patterned substrates is also proposed, in which a specific interaction with particles/polymers directs them into the pre-defined pattern [14–16]. These approaches, however, require direct modification of substrate surface, and accordingly the material type of the substrate is limited. Celio et al. and Harris et al. enabled the colloidal patterning of a flat substrate without topological or chemical pre-modification by introducing a template mask set above the substrate to control solvent evaporation, thereby avoiding this problem, which they call confined dewetting lithography or evaporative lithography [17,18]. However, this approach still encounters a critical problem that any desired change in pattern periodicity or morphology requires another template mask that needs to be created by costly and complicated top-down lithography techniques. In that respect, a template-free or lithography-free self-assembly technique is strongly required to realize controlled fabrication of patterned structures of colloidal particles.

As a possible candidate for the template-free fabrication, it has been demonstrated that the dewetting of a thin liquid film can yield several patterns composed of particle aggregates, such as stripes [19–21], "spoke"-like radial shapes [19], dot arrays [20,22–24], and polygonal patterns [25], owing to the fingering instability [26] or Rayleigh instability [27]. However, the dewetting process is very sensitive to experimental conditions and accordingly poses difficulties in controlling resultant structures. Another template-free process is contact line pinning and subsequent slip motion to produce patterned structures of particles such as ring-shaped patterns on horizontally placed substrates [28–31], known as "coffee stain" patterns [32], and stripe patterns on vertically suspended surfaces in a suspension [33–35]. For the stick-and-slip motion to occur, it is said that the wettability of the substrates is quite important; partially wet substrates are favorable, while easily wettable substrates do not induce the stick-and-slip motion of the contact line [34]. With regard to the stick-and-slip motion, a critical problem in controlling the surface pattern is that the time required for the contact line to remain stuck until the next slip occurs is unavailable a priori because of its stochastic nature, leading to difficulties in predicting the periodicity of the structures. Another problem in the stick-and-slip motion is that the resultant stripes often show distorted shapes and a low degree of periodicity, although several elegant techniques recently reported have made it possible to produce well-defined patterns by successfully controlling the stick-and-slip motion in confined geometries [36–39].

The difficulty in controlling and modeling the dewetting process or stick-and-slip motion stems from the uncertainty of the contact line motion due to the inherent instability of the meniscus. Instead of partially wet substrates, the use of well wet substrates on which fluids spread stably can avoid the problem regarding the uncertainty of the meniscus motion, and more importantly, patterned structures can spontaneously form even on completely wetting substrates. In fact, while studying the formation of *continuous* particulate film by a vertical-deposition self-assembly process called the convective self-assembly method [40], we unexpectedly noticed emergence of stripe patterns on hydrophilic substrates. As a matter of fact, very few studies was succeeded in preparing pattern structures on solvophilic substrates [41]; in addition, the formation mechanism of such patterns was not clarified.

The finding of the stripe pattern formation showed us the potential of the combination of the vertical deposition process with wettable substrates as a template-free pattern formation technique, and highly motivated us to further investigate the convective self-assembly process. Through the investigation, we have revealed excellent performance of the process to spontaneously produce patterned structures of particles on flat substrates, and found out that the key factor in controlling the pattern is the behavior of the meniscus tip at which particulate films form. In this invited review paper, we first overview the convective self-assembly technique, and then introduce our recent results on pattern formation of colloidal particles by using the technique.

2. Convective self-assembly

The convective self-assembly technique is proposed by Dimitrov and Nagayama in 1996 to produce a monolayer composed of the close-packed structure of particles [40], which is based on their precedent experimental investigation on "nucleation" of a close-packed structure of particles [42]. This technique features the control of the homogeneous growth of particle arrays on the basis of a model equation derived from a mass balance in the film formation region. The equation is demonstrated to apply to multi-layer film formation [43]. The schematic of the experimental setup we used is shown in Fig. 1a. In this process, a well-wetted substrate is immersed vertically into a colloidal suspension and the temperature is controlled to allow the solvent to evaporate. As the liquid level descends because of evaporation, the substrate becomes dry and a particulate film appears on the substrate. A basic principle of the particle assembly is as follows. The evaporation rate around the tip of the meniscus formed on a well-wet substrate is larger than that of the bulk solvent owing to the heat transfer from the substrate. As shown in Fig. 1b, evaporation at the meniscus tip induces an upward convective flow to compensate the amount of the solvent evaporation. The convective flow then carries particles into the meniscus tip, at which the assembled particles form a close-packed particle array due to the laterally acting capillary force between the particles. By appropriately adjusting the experimental parameters such as particle concentration, humidity, and temperature as required by the operating window of parameters, this technique can produce uniform particulate films [44] and thus has been applied to various fields [45]. This technique is applicable to a wide range of particle size and type as long as the particles are stably dispersed in a solvent. As for the particle shape, not only spherical particles but also cubes [46], polyhedrons [47], nanoplates [48], nanowires [49,50], nanotubes [51,52], sheets [53,54] can be assembled on a substrate. However attention should be paid to the use of particles with high density and/or large size because this technique transfers particles against gravity. In the case of the silica particle, we have confirmed that the effect of gravity is negligible for the particle size less than 500 nm. Thus for the assembly of larger size of particles,

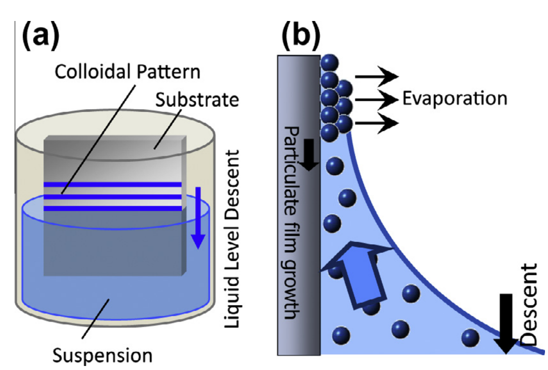

Fig. 1. (a) Schematic illustration of the convective self-assembly technique. (b) Magnified schematic around the meniscus tip.