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Self-Assembly of Colloidal Particles on a Patterned Surface with Wettability

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We have shown a self-assembly of colloidal particles in a two-dimensional structure on a patterned surface with wettability. The assembling process relies on the wettability change of a liquid crystal (LC), used as a colloidal suspending medium, on an alignment surface with varying the ultraviolet exposure. A close-packed structure of the colloidal particles was obtained by adjusting the diameter of the wetting area relative to the particle size and the strength of the wettability. The self-assembling technique would be applicable in various fields of microphotonics and health sciences.

Keywords: close-packed structure; colloidal particles; self-assembly; wettability

INTRODUCTION

A self-assembly of colloidal particles in a two- or three-dimensional structure on a periodically patterned substrate has attracted great attention because of its potential applications to photonic crystals [1,2], catalysts [3], and biochips and sensors [4]. Especially, due to growing needs in life sciences and biomedical industries for creating microarrays of particles functionalized with various kinds of biochemical compounds [5], the integration techniques of the particle assembly become very important these days.

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Recently, a number of attempts have been reported for producing a particle assembly onto a physically well-confined structure prepared by patterning photoresist or polymer on glass substrates [6,7]. In addition, chemically modified surfaces were prepared with a microcontact printing method of patterning alkanethiols on gold substrates [8,9]. Such patterning techniques involve difficult and complex processes. In contrast, the irradiation of an ion beam [10] or the ultraviolet (UV) light [11] can easily modify the surface characteristics including wettability so that the particles can be assembled into ordered structures with no additional processes.

In this work, we show a self-assembly of colloidal particles into a two-dimensional structure on an UV patterned surface. The surface properties such as the LC alignment and the contact angle of the LC droplet varied with the UV illumination. Compared to the evaporation of a solvent such as water [7], ethanol [11], and toluene [12], our approach utilizes the LC as a non-evaporable suspension medium whose surface tension is sufficiently high to assemble colloidal particles within the LC droplets into a highly close-packed structure. The main idea is that the dimension of the LC droplet relative to the particle size determines the structural arrangement of the particles because the particles located at an outmost boundary of the LC droplet deform the droplet surface, and thus the asymmetric surface tension [9,13] generates the horizontal force to move particles towards the center of the droplet.

EXPERIMENTAL

The self-assembling process is schematically illustrated in Figure 1 where the LC alignment layer is patterned using the UV exposure through a photomask. As the UV illuminated regions undergo chemical modifications, they become relatively wet whereas other regions remain intact.

A homeotropic LC alignment agent, JALS 684 (Japan Synthetic Rubber), was spin-coated on the glass substrate at the speed of 3000 rpm for 30 sec, followed by thermal curing at 160°C for 1 h. Then, unpolarized UV light was selectively illuminated through a photomask to generate the spatially different wettability on the surface. In order to check the surface characteristics, contact angles were measured for several different illumination times (0, 1000, 2000, and 3000 sec) at the intensity of 94 mW/cm². The variation of the contact angle of the LC droplet originates from the altered interaction [14] between the LC molecules and the patterned alignment layer.

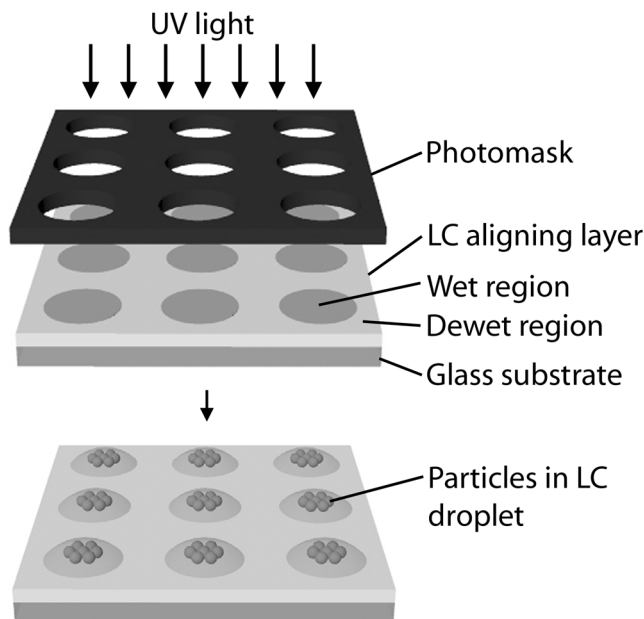


FIGURE 1 The schematic diagram of the formation of an array of droplets containing assembled particles on the patterned surface with wettability through the UV illumination.

This was examined in the LC cell (6 μm thick) with no particles by observing the distribution of the LC director.

For self-assembling colloidal particles on the prepared substrate, a commercial LC of 5CB (Aldrich) containing polystyrene particles (Molecular Probes, Eugene, OR) was placed on the patterned surface and forced to spread throughout the substrate. The clearing temperature of 5CB is 35°C. An array of the LC droplets containing assembled particles each was obtained on the wet regions.

RESULTS AND DISCUSSION

The surface properties of the LC alignment layer were investigated by measuring contact angles of the LC droplets as a function of the UV illumination time and observing the LC alignment. According to Young's equation [15], the contact angle is described as $\cos \theta = (\gamma_{sv} - \gamma_{sl})/\gamma$, where γ_{sv} , γ_{sl} , and γ represent the solid–vapor, solid–liquid, and liquid–vapor surface energy per unit area, respectively. This means that solid–liquid surface energy of the LC alignment layer

decreases with increasing the UV illumination time. Figure 2(a) shows the contact angles of the LC droplet on the LC alignment layer as a function of the UV illumination time. As the illumination time increases, the contact angle decreases and eventually reaches the saturation value of 15° . The change in the contact angle is reflected

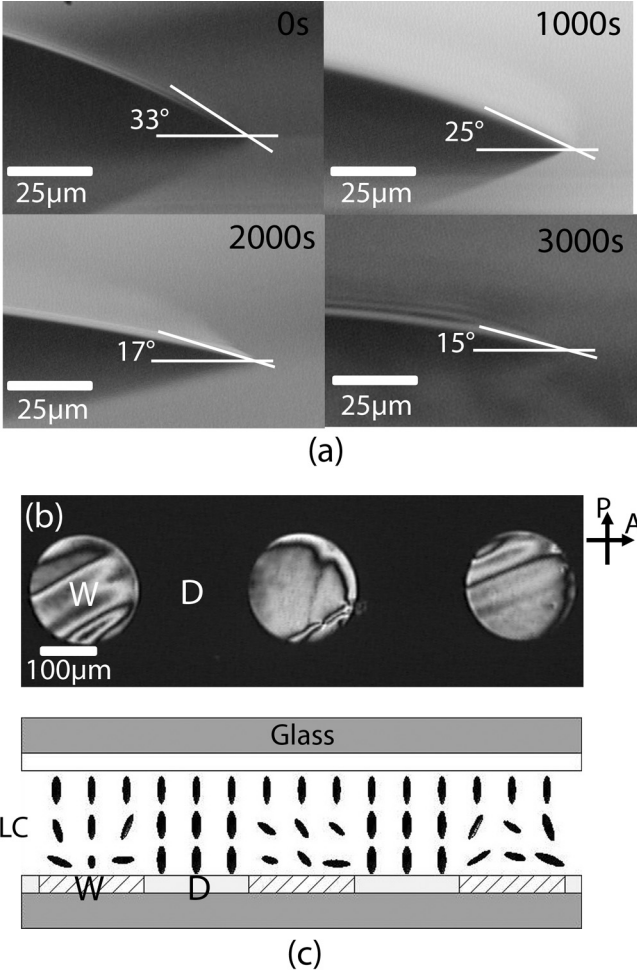


FIGURE 2 (a) The microscopic images of the contact angles of 33° , 25° , 17° , and 15° of the LC droplets after the UV illumination for 0, 1000, 2000, and 3000 sec, (b) the microscopic textures of the LC on UV patterned substrate under crossed polarizer, and (c) the LC alignment corresponding to (b).

in the LC alignment as shown in Figure 2(b) that are microscopic textures of the LC in the UV illuminated regions (circular wet regions) and dark homeotropic regions. The wet and homeotropic regions were denoted by W and D , respectively. Note that there is no preferred direction of the LC molecules in the UV illuminated region of W . This indicates that the surface undergoes chemical modifications so that the LC aligning capability disappears upon the UV irradiation. The regions of D and W match with dewet and wet regions depicted in Figure 2(c), respectively. Note that the difference of the surface energy between D and W plays an essential role in forming spontaneously the LC droplets on the patterned substrate. In other words, a self-assembly of colloidal particles in the LC medium can be developed when the surface energy difference between the two regions (D and W) reaches a certain value as the UV illumination time increases.

Figure 3(a) shows a microscopic image of the LC droplet which contains polystyrene particles of $10\mu\text{m}$ in a wet circular region of

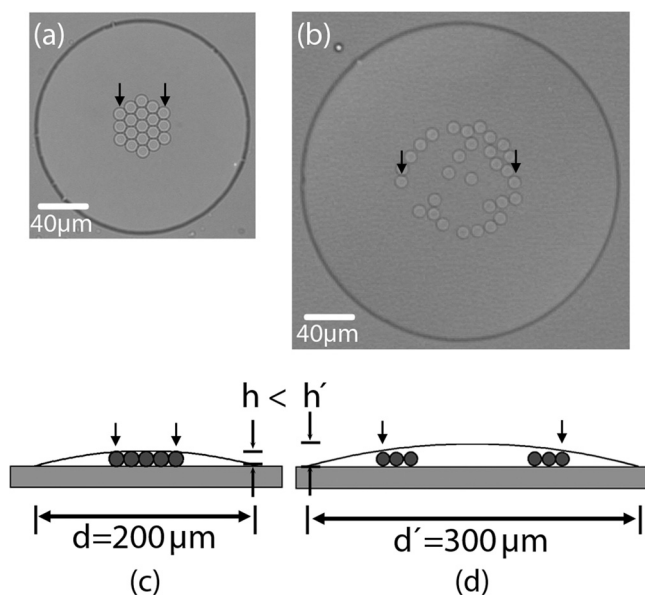


FIGURE 3 The microscopic images of droplets containing the particles of $10\mu\text{m}$ in diameter within the circular wet regions of (a) $200\mu\text{m}$ and (b) $300\mu\text{m}$. The cases of (c) and (d) correspond to (a) and (b), respectively. A set of two arrows in each figure indicate the contact lines of the outmost particles in each droplet.

the 200 μm in diameter. All the particles were located in the central region within the droplet to form a highly close-packed structure. The height of the circular droplet depends on the radius and the contact angle according to $\tan(\theta/2) = h/r$. Here, h and r represent the height and the radius of the droplet, respectively. Figure 3(c) represents the physical mechanism for the particle assembly shown in Figure 3(b). A set of two arrows indicate the contact points of the outmost particles in each droplet. Since the measured contact angle is 15° , the height of the droplet calculated from the above equation is about 13.2 μm . This is slightly greater than the diameter of the particle (10 μm). The outmost particles tend to deform the droplet surface, and thus the asymmetric surface tension will generate the horizontal force to move the particles towards the center of the droplet. This is clearly seen in Figure 3(b) where only the diameter of the droplet was increased to 300 μm , maintaining both the particle size and the contact angle the same as in Figure 3(a). Figure 3(d) shows the schematic diagram of the particle assembly. The height of the droplet is estimated as 19.7 μm , which is almost two times greater than the particle size. In this case, the particles were located only in the circular peripheral region where the asymmetric surface tension tends to move the particles as far as possible.

CONCLUSION

We have developed a simple and versatile process of assembling the colloidal particles in a close-packed structure. The particles suspended in the LC were spatially placed on a circularly patterned wet surface with UV in a spontaneous way. The close-packed structure of the colloidal particles was obtained by adjusting the height of the droplets to the particle size. This system would be very useful for application in the various fields including microphotonics and biomedical sciences.

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