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Colloidal Assembling Template with Wrinkled Patterns Based on Liquid Crystalline Polymer

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Colloidal microwires are constructed using anisotropic assembling templates with periodically wrinkled patterns of a liquid crystalline polymer (LCP). The wrinkled LCP patterns with the period of a few micrometers are produced from reactive mesogens on an alignment layer by the oxygen plasma treatment and used for assembling colloidal particles into microwires through a simple slit-coating process. A two-directional assembly of the colloidal particles is also demonstrated on the LCP template with two stamping-assisted rubbing directions. Our approach to the colloidal assembly is applicable for building up advanced photonic and optoelectronic devices.

Keywords reactive mesogen; liquid crystalline polymer; wrinkled patterns; colloidal assembly; colloidal microwires

1. Introduction

Reactive mesogens (RMs) have been widely used for many electro-optical applications [1–4] and displays [5–7] due to their capability of constructing polymer networks with optical anisotropy. The use of the RMs has been primarily focused on tuning the electro-optical properties at a mesoscopic level through doping in host materials such as liquid crystals (LCs) [4,7–9]. Furthermore, the intrinsic anisotropic mechanical properties of the RMs associated with the molecular order enable to produce functional liquid crystalline polymer (LCP) systems showing structure transformation [10–12], shape memorization [13–15], and surface topographies [16–18]. Among them, the wrinkled patterns of the LCP [17,18] have great potential for more sophisticated templates owing to the easy control of direction and the simplicity of fabrication through the directional alignment of the RMs. Most of the previous works were carried out toward achieving the anisotropic elastic properties on the elastomers in bilayer structures through the stretching and releasing processes [19–22].

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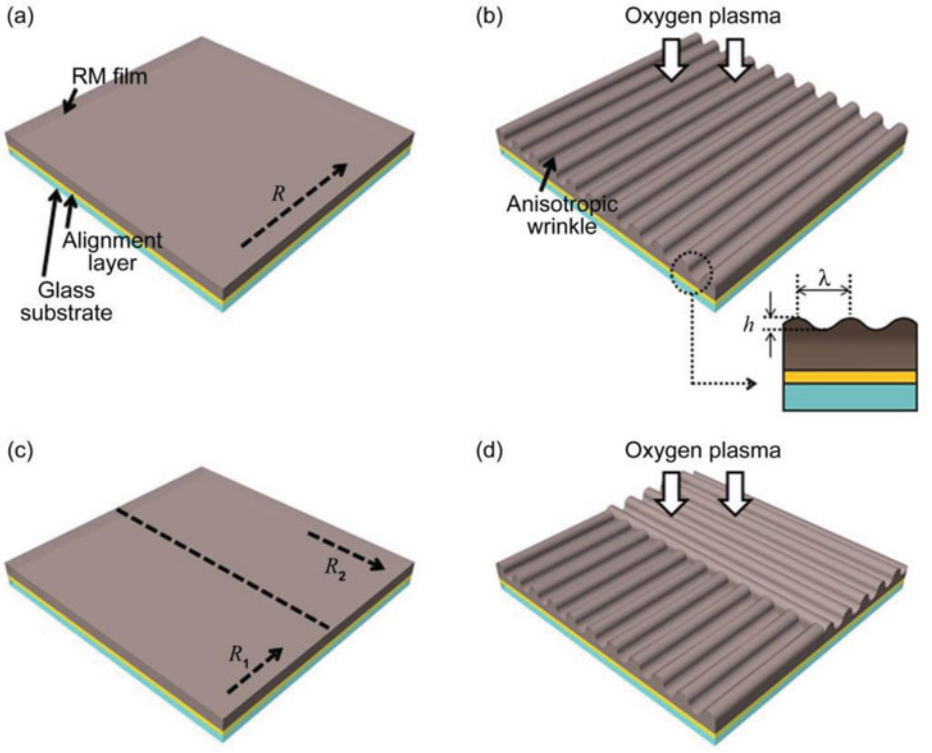

Figure 1. Schematic diagram showing the fabrication steps for the templates with the wrinkled patterns of the LCP: (a) RMs on an alignment layer with one rubbing direction (R), (b) anisotropic one-directional wrinkled patterns by oxygen plasma treatment together with the wrinkle geometry, (c) RMs on an alignment layer with two rubbing directions (R_1 and R_2), and (d) anisotropic two-directional wrinkled patterns by oxygen plasma treatment. The height and the period of the wrinkle are represented by h and λ, respectively.

Here, we demonstrated colloidal microwires constructed using anisotropic assembling templates with periodically wrinkled patterns of the LCP. The wrinkled patterns were produced through polymerization of the RMs on an alignment layer by the oxygen plasma treatment [17]. According to the guidance of the wrinkled patterns, polystyrene (PS) particles in colloid were self-assembled into microwires through a simple slit-coating process. The dimension of the microwires was found to be predominantly governed by the periodicity of the wrinkled pattern in relative to the particle size. A two-directional assembly of the colloidal particles was also fabricated on the LCP template with two stamping-assisted rubbing directions [23]. This bottom-up approach is a versatile method of constructing diverse colloidal assemblies.

2. Templates with Wrinkled Patterns of LCP

Figure 1 shows a schematic diagram of the fabrication steps for the templates with the wrinkled patterns of the LCP. For the homogeneous alignment of the RMs, a polyimide (PI) solution (AL22620, Japan Synthetic Rubber Co.) was first spin-coated on a glass substrate at

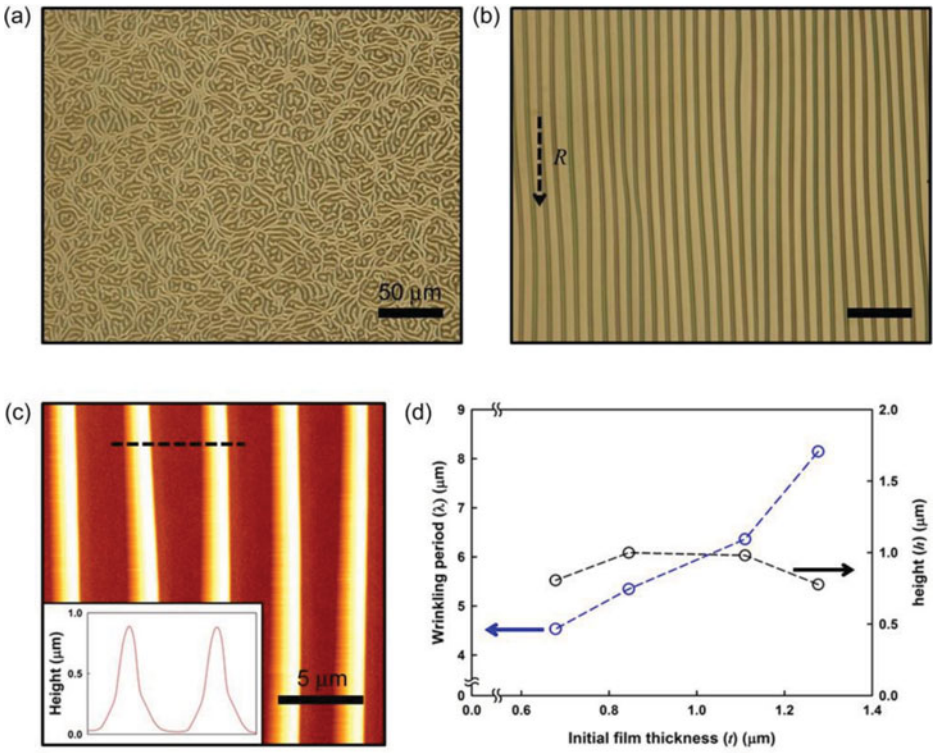

Figure 2. The microscopic images of the wrinkle patterns: (a) random patterns of the LCP on the unrubbed PI layer, (b) regular one-directional patterns on the rubbed PI layer along the rubbing direction R, (c) the AFM image of a few wrinkled patterns of the LCP formed on the rubbed alignment layer. The inset shows the surface profiles of two patterns, and (d) the wrinkle period (blue dashed line) and the wrinkle height (black dashed line) variations with the initial thickness of the RM film.

the rate of 3000 rpm for 30 s and then thermally cured at 180°C for 1 h as shown in Fig. 1(a). The alignment layer was subsequently rubbed along the direction of R. The RM solution used in this work was a propylene glycol monomethyl ether acetate solution containing four different acrylate-based mesogenic monomers: 4-(6-acryloyloxyhexyloxy)-benzoic acid (4-cyanophenyl ester), 4-(3-Acryloyloxypropyloxy)-benzoic acid 2-methyl-1,4-phenylene ester, 4-(6-Acryloyloxyhexyloxy)-benzoic acid-(4-methoxyphenylester), and 2-methyl-1,4-phenylene-bis[4-(6-acyloyloxyhexyloxy)benzoate] (RMS03-001C, Merck) [24] and it was spin-coated on the rubbed PI layer at the rate of 2000 rpm for 30 s. By the oxygen plasma treatment at the intensity of 150 W under 0.1 torr for 30 s, the RMs were polymerized to produce anisotropic wrinkles along R as shown in Fig. 1(b). This wrinkling behavior can be understood in terms of a buckling instability in a bilayer structure [25]. The RM film is assumed to be a bilayer structure which is represented by a heavily polymerized thin layer supported on a weakly polymerized underlayer during the oxygen plasma treatment. The height (h) and the period (λ) of the wrinkle will depend on the conditions for the plasma treatment as well as the initial thickness of the RM film. The fabrication of a two-directional template with two rubbing directions (R_1 and R_2) was shown in Figs. 1(c) and 1(d). Two different alignment directions were produced in two steps through the stamping-assisted rubbing process combined with a sacrificial layer [23].

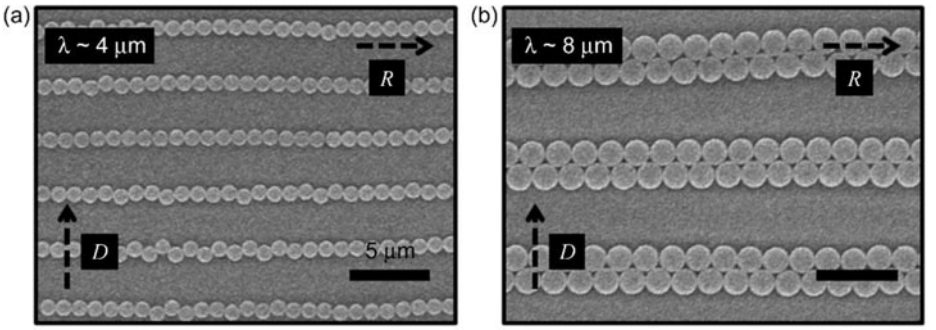

Figure 3. The SEM images of an array of the colloidal microwires: (a) the colloidal microwires with the width of 1 μm (single lines of the PS particles of 1 μm in diameter) and (b) the colloidal microwires with the width of 4 μm (double lines of the PS particles of 2 μm in diameter).

Before constructing the colloidal assemblies in microwires on the templates, we describe the topography of the wrinkles of the LCP and the dependence on the initial thickness of the RM film. Random patterns of the LCP were observed on the entire area of the unrubbed PI layer as shown in Fig. 2(a) whereas regular one-directional patterns along the rubbing direction *R* were clearly developed as shown in Fig. 2(b). This means that a long-range anisotropic force on the rubbed PI surface plays a critical role in aligning the RMs so as to produce the wrinkled patterns of the LCP through polymerization by the oxygen plasma treatment. A typical image of a few wrinkled patterns of the LCP, observed with an atomic force microscope (AFM), was shown in Fig. 2(c). The surface profiles of two patterns of about 1 μm high were shown in the inset. This structural undulation is primarily related to the stress relaxation in a thermally-induced swelling model [26]. In this model, the increase of the initial film thickness (t) results in the increase of the height (h) and the period (λ) of the wrinkled pattern. While λ was found to monotonically increase with t, h was weakly dependent on t as shown in Fig. 2(d). This may be attributed to a relatively small thickness of the underlayer compared to λ and/or a low power of oxygen plasma.

3. Construction of One-directional Microwires

For fabricating colloidal microwires, the PS particles dispersed in water (Duke Science) were deposited on the templates by slit-coating along the direction (D) perpendicular to R at the speed of 25 μm/s. Figures 3(a) and 3(b) show the images of self-assembled colloidal microwires with the width of 1 μm (single lines of the PS particles of 1 μm in diameter) and 4 μm (double lines of the PS particles of 2 μm in diameter), respectively, obtained with a scanning electron microscopy (SEM) [27]. As described above, it is clear that λ is governed by the initial thickness (t) of the RM film. The value of λ can be easily varied in a range of a few micrometers with varying the spin-coating rate for the RM solution. Two RM films were prepared at two different rates of 1000 rpm and 6000 rpm for 30 s. For the case of 1000 rpm, t was measured to be about 0.7 μm and λ was about 4 μm while for the case of 6000 rpm, t was about 1.5 μm and λ was about 8 μm. The magnitude of λ may be achieved by adjusting the RM concentration in solution. Depending on the period λ and the size of the PS particle, colloidal microwires in either single lines or double lines were produced as shown in Fig. 3. Note that the uniformity of the colloidal microwires depends on the slit-coating speed. Below a critical value of the slit-coating speed, the colloidal particles

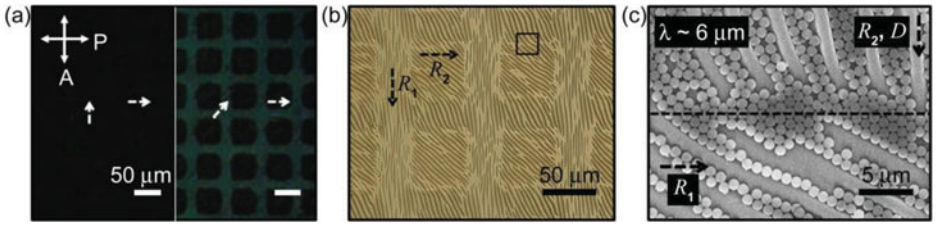

Figure 4. (a) The optical microscopic images of the LC texture aligned along two different rubbing directions, being perpendicular (left) or oblique (right) to each other. The polarizer and the analyzer are denoted by P and A. White dashed arrows represent the rubbing directions on the bottom surface of the cell. (b) The optical microscopic image of the two-directional wrinkle pattern. The area enclosed by the open black square corresponds to the SEM image shown in Fig. 4(c). (c) The SEM image of two-directional colloidal microwires.

are closely packed above the hills of the wrinkles to form multilayer structures [28]. The slit-coating direction along R tends to produce the voids of the particles in lines.

4. Construction of Two-directional Microwires

The template for assembling the PS particles into two-directional microwires was prepared using two stamping-assisted rubbing processes. The RM film being studied was prepared at the spin-coating rate of 3000 rpm for 30 s and treated with the oxygen plasma at the intensity of 150 W under 0.1 torr for 30 s. The period of the wrinkles was measured to be about 6 μm.

Let us first examine the LC alignment along two directions defined by two successive stamping-assisted rubbing processes. As shown in Fig. 4(a), a typical nematic LC (E7, Merck) was well-aligned along two different rubbing directions (denoted by white dashed arrows), being either perpendicular or oblique to each other on the bottom surface of the cell (5 μm thick). The top surface of the cell was unrubbed. The alignment layer was the same used for the RMs.

In contrast to the LC case, as clearly seen in Fig. 4(b), the wrinkled patterns of the LCP have two orientations being different to initial rubbing directions after the polymerization of the RMs. One of them coincides with the first rubbing direction (R_1) while the other makes an angle (about 45°) between R_1 and the second rubbing direction R_2. This is probably due to the relaxation of the excess elastic strain produced during the cross-linking of the RMs that were initially aligned in the orthogonal configuration. In Fig. 4(c), the SEM image showing two-directional colloidal microwires, fabricated using the template with two orientations of the wrinkled patterns of the LCP, is presented. It corresponds to the area enclosed by the open black square in Fig. 4(b). The colloidal particles were substantially accumulated near the domain boundaries that were poorly defined since two different wrinkles patterns, being oblique to each other, were not well distinguished.

5. Conclusion

We demonstrated the templates with anisotropic wrinkled patterns of the LCP for assembling colloidal particles. The wrinkled patterns were formed in the aligned RM film through polymerization by the oxygen plasma treatment and used for fabricating colloidal microwires through a simple slit-coating process. Depending on the height and the period

of the wrinkle in relative to the particle size, a wide range of microwires in single lines or double lines can be produced. Moreover, the templates with multiple orientations of the wrinkled patterns, in principle, enable to construct complex networks of colloidal particles. This work will provide a new platform for the bottom-up fabrication of diverse photonic and optoelectronic devices.

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