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Spiral Alignment of Fullerene Microcrystals via Dewetting

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We demonstrate the autonomous formation of spiral patterns made of fullerene C_{60} microcrystals via dewetting process on a solid substrate. We also succeeded in enlarging the spiral size by introducing a pillar that worked as an artificial core of the spiral. In situ observation of spiral formation revealed the stable inbound rotation of the pinning front about the meniscus region close to the pillar. The spacing ratio of the spiral, $R(\theta)_{n+1}/R(\theta)_n$, was 1.2,which indicates the formation of a logarithmic spiral.

Keywords Dewetting; dynamic self-assembly; fullerene C_{60}; microcrystals; pattern formation; spiral

1. Introduction

Dynamic self-assembly in chemical systems has a wide range variety such as formation of periodic precipitation known as Liesegang bands [1,2] and depositions of coffee stain associated with solvent evaporation [3,4]. In particular, arrangement of particle arrays from colloidal suspension via evaporation process has been widely studied by using micro- to nano-particles [5,6], polymers [7,8], DNA [9], and a mixture of polymer and metal nano-particles [10]. The aggregates are generated by the pinning and the capillary flow of the solution, which occurs close to the moving three phase line (TPL) [11]. As the interfacial deformation develops by solvent evaporation, the liquid film shows a periodic motion which is called stick-slip motion to result in a periodic arrangement of the aggregates [8]. Thus, the size and the spacing of the colloidal aggregates strongly depend on the shapes of the meniscus at the dewetting region [12].

In this article, we report a novel dewetting pattern from a dilute solution of a molecule with a spherical symmetry: fullerene C_{60}. Though C_{60} is known to have

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crystal polymorphisms [13], our interest is focused on a macroscopic symmetry-breaking phenomenon in the dewetting pattern, i.e., the formation of spiral patterns out of C_{60}.

2. Micro-Spirals in Spontaneously Dried-Up Pattern

Experimental procedures in common are as follows: Fullerene C_{60} (99.5%, Aldrich) and toluene (analytical grade, Wako chemicals) were used without further purification. Fullerene were dissolved into toluene under ultrasonic bath (temperature = 9∼14°C). The solutions were filtrated through the pore size of 0.22 μm before use. Glass plates (S-1214, Matsunami, Japan) used as solid substrates were cleaned by exposure of UV/O_3 for 2 hours and rinsed with ethanol followed by drying under air flow. The patterns made of fullerene microcrystals were observed under optical microscope (Olympus IX-70, Olympus, Japan) equipped with a high-speed camera (VW-6000, KEYENCE, Japan), and under laser microscope (VX-9700, KEYENCE, Japan).

A droplet of a toluene solution of fullerene C_{60} was placed on a glass plate. When the concentration of C_{60} was 0.10 wt% (or below), the TPL of the thin liquid film receded towards the center of the droplet with a stick-slip motion, resulting in the formation of the bands of C_{60} microcrystals (Fig. 1(a)). In contrast, from the solution whose concentration was higher than 0.50 wt%, dense bands appeared at the edge of the droplet; no stick-slip motion but the trace of advective flows was recorded in the droplet area (Fig. 1(b), (c)).

In a center region of the droplet, fullerene microcrystals were occasionally patterned into concentric rings, or into spirals (Fig. 2(a)–(d)). Among 52 spirals observed, 27 were dextral and 25 were sinistral. Since there are no external factors to control the directions of the spirals in this system, they should be racemic. The most probable structure of the C_{60} microcrystals is fcc, which is suggested by the X-ray diffraction analysis.

Figure 2(a) shows the relation between the logarithm of the distance R of each microcrystal from the spiral center and the rotational angle θ ($=\omega/2\pi$). This analysis reveals that the microcrystals are aligned in a logarithmic spiral with the following relation: $\ln R = b\theta + \ln a$, where both a and b are constants. In other words, the ratio of spacing is constant: R_{n+1}/R_n ($=ae^{b(\theta+2\pi(n+1))}/ae^{b(\theta+2n\pi)} = e^{2\pi b}$), where θ is kept

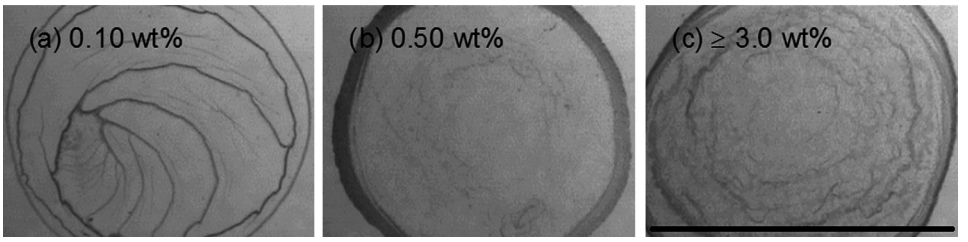

Figure 1. Macroscopic dried-up patterns out of C_{60}/toluene droplets on glass substrate ($T = 27.7 \pm 0.1$°C; relative humidity = 67.3 ± 0.2%). (a): A dried-up pattern with a global stick-slip motion of the three phase line. (b) and (c): Dried-up patterns of microcrystals, which look like a coffee stain without the stick-slip motion. Scales in (a)–(c) are the same (the bar in (c) is 8 mm).

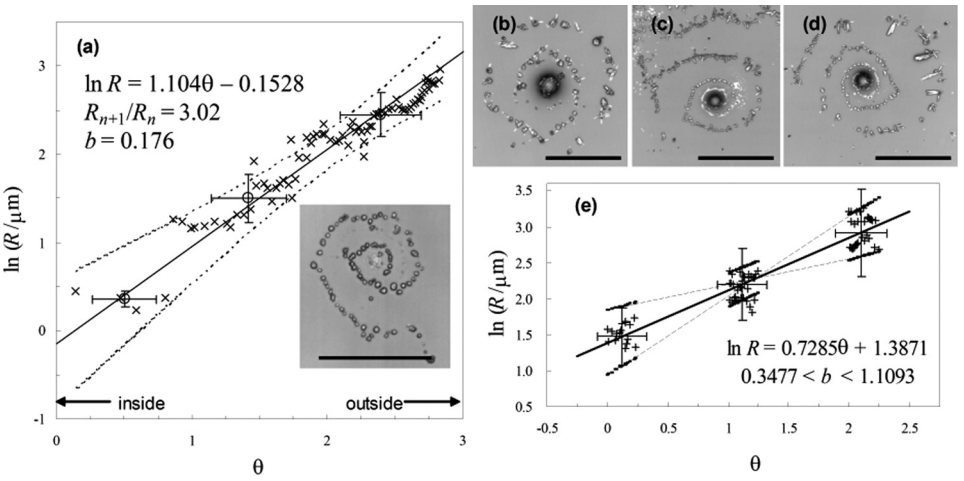

Figure 2. Geometrical characteristics of microscopic spirals observed after dried-up of 1.15 wt% C_{60}/toluene droplets (5 μL on glass substrate). (a): An analysis of each C_{60} microcrystals in a spiral shown as the inset. R and θ are the distance and the angle of rotation, respectively, in polar coordinate. (b)–(d): Spirals in other dried-up patterns. (e): A statistical analysis of spirals (b)–(d) in the first quadrant regions. Error bars mean the standard deviations ($\pm 3\sigma$). Dotted curves in (a) and (e) are 95% confidential interval (95% CI). Broken lines in (e) indicate the minimum and the maximum slopes ($d\ln R/d\theta$) with 95% CI. Black bars in images stand for 50 μm.

constant. This relation is all the same as the spacing rule of Leasegang phenomenon [2,3]. The specific angle of the present logarithmic spirals was the same and was about 0.467π (84°) (Fig. 2(e)), suggesting the same formation mechanism existed behind.

On fluorinated surfaces such as PFA (NEOFLON®, Daikin Ind., Ltd., Japan) and PTFE (NAFLON®, NICHIAS Corp., Japan), the liquid film of a C_{60}/toluene solution was hard to spread, and no spirals were induced. In these cases, fullerene molecules were crystallized at the edge of the droplet all the same as in Figure 1(b). The value of contact angle of the toluene solution on the glass plate was close to zero (about 0.5°), and 31.5° and 33.9° on NEOFLON® and NAFLON®, respectively. This result suggests the importance of the wettability (or the thickness) of the solution for the spiral formation of C_{60} microcrystals.

3. In Situ Observation of Macro-Spiral Formation

A droplet of fullerene C_{60}/toluene was dried up with a stainless pillar ($d = 250$ μm). The position of the pillar was the center of the droplet, and was faced on a glass substrate.

Through the evaporation of toluene, the microcrystal bands were formed around the pillar (Fig. 3(a)). The outer bands ($r > 300$ μm) were concentric rings, and the inner was spiral. The dewetting velocity in the inner region was about 2.7 times faster than the outer one (see the inset in Fig. 3(a)). The rate of the distances between the neighboring bands, R_{n+1}/R_n, is biphasic (Fig. 3(b)). That is, the rate is quadratic in the outer region covered with concentric rings and the spiral (broken

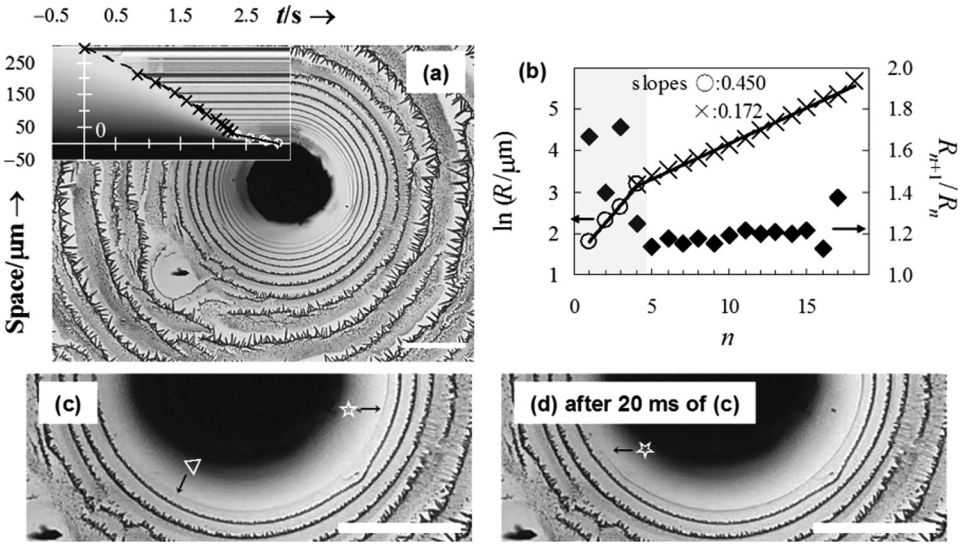

Figure 3. In situ observation of a macroscopic spiral formations, and the geometrical analysis. (a): A dried-up pattern of C_{60}/toluene droplet with a pillar (a large black circle; $d = 250\,\mu m$). The inset is a spatio-temporal pattern along the radial direction at 90°. The black horizontal lines are bands of the microcrystals. (b): Analysis of (a) by semi-logarithmic plots of the distance from the center to each band at $n\pi/2$ (○ and ×), and the band spacing (◆). (c) and (d): Snapshots at 1.83 s and 20 ms after (c), respectively. Both the pinning front (stars) and rupturing front (triangle) rotated counterclockwise steadily. White bars are 200 μm in all images.

curve and ×), whereas it is linear in the inner region with microstructures (solid line and ○). The ratio R_{n+1}/R_n is constant to be 1.2 for the outer concentric rings and the spiral (Figure 3(b)). In situ observation revealed the stable inbound rotation of the pinning front about the meniscus region close to the pillar (Fig. 3(c), (d)). Therefore we can say that this is an extraordinary spiral growing from outside toward inside, i.e., growing in the opposite way from the commonly observed logarithmic spirals in biological systems.

4. Conclusions

We demonstrated the formation of a discretely and continuously aligned logarithmic spiral pattern composed of fullerene C_{60} microcrystals on a solid substrate via dewetting of a C_{60} solution. Spiral formations assisted by a pillar revealed the inbound growth of a logarithmic spiral and suggested the practical way to form a macroscopic spiral patterns made of C_{60} microcrystals.

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