Hindawi
Advances in Condensed Matter Physics
Volume 2018, Article ID 9795654, 9 pages
https://doi.org/10.1155/2018/9795654

Research Article

Enhanced Coffee-Ring Effect via Substrate Roughness in Evaporation of Colloidal Droplets

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Received 17 January 2018; Accepted 1 April 2018; Published 7 May 2018

Academic Editor: Yuri Tarasevich

The analysis of dried drop patterns has various applications in research fields like archeology, medical practice, printing, and so on. In this paper, we studied the evaporation and pattern formation of polytetrafluoroethylene (PTFE) colloid droplets on smooth substrate and rough substrates with different roughness. We found that the evaporation of droplets shows remarkable coffee-ring effect on smooth substrate and that the cross-section of the ring is wedge-shaped with its thickness decreasing from the edge to the center. However, with increasing roughness, the effect strengthened, with the section of the coffee-ring changing from wedge- to hill-shaped. The contact angle decreased with increasing roughness, leading to an increase in evaporation rate. Moreover, wicking led to additional evaporation, which also enhanced capillary flow, moving more particles to the edge. In addition, the rough structure of the substrate inhibited the back-flow of the capillary flow, preventing the particles' move to the center. The formation of radial wrinkles on the edge also led to particle retention, preventing them from moving to the center. All these factors contribute to the decreased width and increased height of the coffee-ring pattern after evaporation on rough surfaces. It is an effective method to regulate the deposition pattern of evaporating droplet by changing the substrate roughness.

1. Introduction

Droplet evaporation is one of the most common physical phenomena occurring both in nature and in many industrial processes [1, 2]. Droplets containing relatively little volatile substance always form complex patterns after evaporation [3, 4]. Many studies have been conducted to understand the formation mechanism of the coffee-ring effect, as well as the formation of cracks in the patterns and ways to regulate this process. In 1997, Deegan et al. [5], who first revealed the mechanism of coffee-ring pattern formation via colloidal droplet evaporation, noted the important role of capillary flow on mass transport caused by uneven evaporation. Thereafter, many research groups studied the regulation of coffee-ring effect in different ways [6–9], including changing the shape of the suspended particles, adjusting the PH value of the dispersion, and using electrowetting method of controlling the movement of the contact line. In a recent study, the coffee-ring effect was effectively suppressed to achieve a uniform deposition of particles by introducing the linear polymer polyethylene oxide (PEO) into SiO_2 colloidal droplets [10].

Another common phenomenon accompanied by droplet evaporation is the appearance of cracks. Sometimes the cracks, especially nanocracks, can serve as a template, for example, the preparation of nanowires [11]. But in most cases, such as the film making, large-area coating, cracks need to be suppressed. Chiu et al. [12] noted that cracks emerge when the deposition pattern thickness exceeds a critical value. Under these conditions, the release of elastic energy can be greater than the dissipated energy of crack formation. A variety of crack pattern morphologies can be formed during droplet evaporation, including spiral [13], wavy like [14], ring-shaped [15], and radial [16]. Boulogne et al. [17] studied the factors affecting crack morphology, such as particle properties, dispersant type, and drying conditions. Recently, we found that, after evaporation, polytetrafluoroethylene (PTFE) colloidal droplets can form radial cracks, owing to the formation of a similarly shaped stress field within droplets during evaporation process, which has been confirmed via formed radial wrinkles during evaporation (confirmed by the formation of radial wrinkles) [16]. Moreover, evaporation of biological drops, such as blood, often leads to interesting crack patterns which contain valuable information for diagnosis [18].

Despite progress being made in regulating the coffee-ring effect and crack formation during droplet evaporation, the methods used often change the nature of the droplet itself, for example, by introducing polymers, inorganic particles, or changing the particle shape, which is unfavorable for producing a high-purity vapor-deposited film. Thus, it is necessary to adopt alternative approaches to regulate droplet evaporation. It has been reported that the substrates play an important role in pattern formation of drying drops [19]. We tried to change the substrate properties but not the droplet composition. This can be achieved by changing only the roughness of the substrate. Currently, there are very few studies of droplet evaporation on substrates with different roughness [20]. Accordingly, the mechanism by which roughness affects crack formation is unclear. To better understand these processes, in the present study we investigate evaporation and the patterns of colloidal droplets on a smooth glass slide substrate and glass substrates with different roughness. We reveal the influence of roughness to droplet evaporation, crack nucleation, and growth mechanism, thus providing a framework for the preparation of multifunctional films using evaporating method.

2. Methods and Materials

2.1. Materials. The colloidal suspension was made by dispersing polytetrafluoroethylene (PTFE) nanoparticles into water with a weight fraction of 60% by sonication for 30 minutes. The average radius of the particles is ~50 nm, with a dynamic viscosity is 6 mm^2/s and a density of 1.5 g/cm^3. The water used in the experiments was purified with an Ultrapure Water System (EPED, China) with a resistivity of 18.25 MΩ·cm. The substrates used in the experiment include smooth glass slide and the glass slide polished by sand paper with different mesh size. In the polishing process, the sand paper was slid three times over the substrates under the same compressive stress. All substrates were cleaned in ultrasonic cleaners filled with alcohol and acetone successively.

2.2. Morphology and Roughness Characterization. The roughness of the substrates and the deposition pattern were measured using a laser scanning confocal microscope (ZEISS, LSM 800). To obtain more information of the morphology and structure of the evaporated deposition, the deposited patterns were studied using a scanning electron microscope (SEM, ZEISS-SUPRA-55). The section of the deposition pattern was also analyzed using laser scanning confocal microscope, confirming the thickness change in the radius direction of the pattern. Static contact angles were determined using the sessile drop method on a contact angle measurement apparatus (Powereach, JC2000D, China).

2.3. Evaporation Experiments. Droplets of the colloidal solution (~0.2 μL) were deposited with a microsyringe (total volume: 1 μL) on the substrate, which was cleaned thoroughly by alcohol and distilled water and dried in a drying oven. The evaporation process and the final deposited pattern were observed using optical microscopy (Olympus, BX51). For the evaporation process, images were recorded by means of a video recorder at 25 frames/s. All the experiments were carried out at room temperature ~22 ± 2°C and at relative humidity of ~45 ± 5%.

3. Results and Discussion

3.1. Roughness and Contact Angle of the Substrate. To study the influence of substrate roughness on the evaporation of the PTFE droplet, we characterized the surface morphology and roughness of the substrate. The results of laser scanning confocal microscopy are shown in Figures 1(a)–1(d) and the corresponding static contact angles on the different substrates are shown in Figures 1(e)–1(h). All the droplets for the experiment were dropped naturally. The static contact angle of the suspension on the smooth substrate was 37°. With increasing roughness, the contact angle decrease, as shown in Figures 1(e)–1(h) (35°, 30°, 27°, and 25°, respectively).

A numerical relationship exists between the roughness and contact angle. In the Wenzel model, $\cos\theta^* = r\cos\theta$, where θ^* is the apparent contact angle of the sessile drop on the substrate, r is the roughness of the smooth substrate, and θ is the intrinsic contact angle (i.e., the contact angle for the ideal smooth substrate). The value of r will increase when the roughness increases and the value of θ is constant. Thus, theoretically, θ^* will decrease when r increases (i.e., the rougher the substrate, the smaller the contact angle). Our experimental results are in agreement with this relationship.

3.2. Evaporation Patterns on Different Substrates. Figure 2 shows the evaporation patterns of PTFE droplets deposited on smooth and rough substrates. The cross-sections of the smooth and rough substrates are shown in Figures 2(c) and 2(f), respectively. On the smooth substrate, the pattern is thicker near the edge and gradually becomes thin toward the center, as can be seen in Figures 2(a) and 2(c). The width of the coffee-ring is about 0.4 mm, which is more than half of the radius of the pattern. Radiating cracks distribute on the coffee-ring. In the center, some nanoparticles are scattered; however, at the center, because the thickness is smaller than the critical value [12], no crack emerges.

The coffee-ring effect is more remarkable on rougher substrates. The cross-section of the coffee-ring exhibits symmetrical hill-like shapes. The thickness of the shape reaches 80 μm with a width of 0.2 mm. The width is about one-third of the radius. Cracks are distributed radially along the coffee-ring. The remainder of the pattern is covered by a few particles, which have not formed cracks yet.

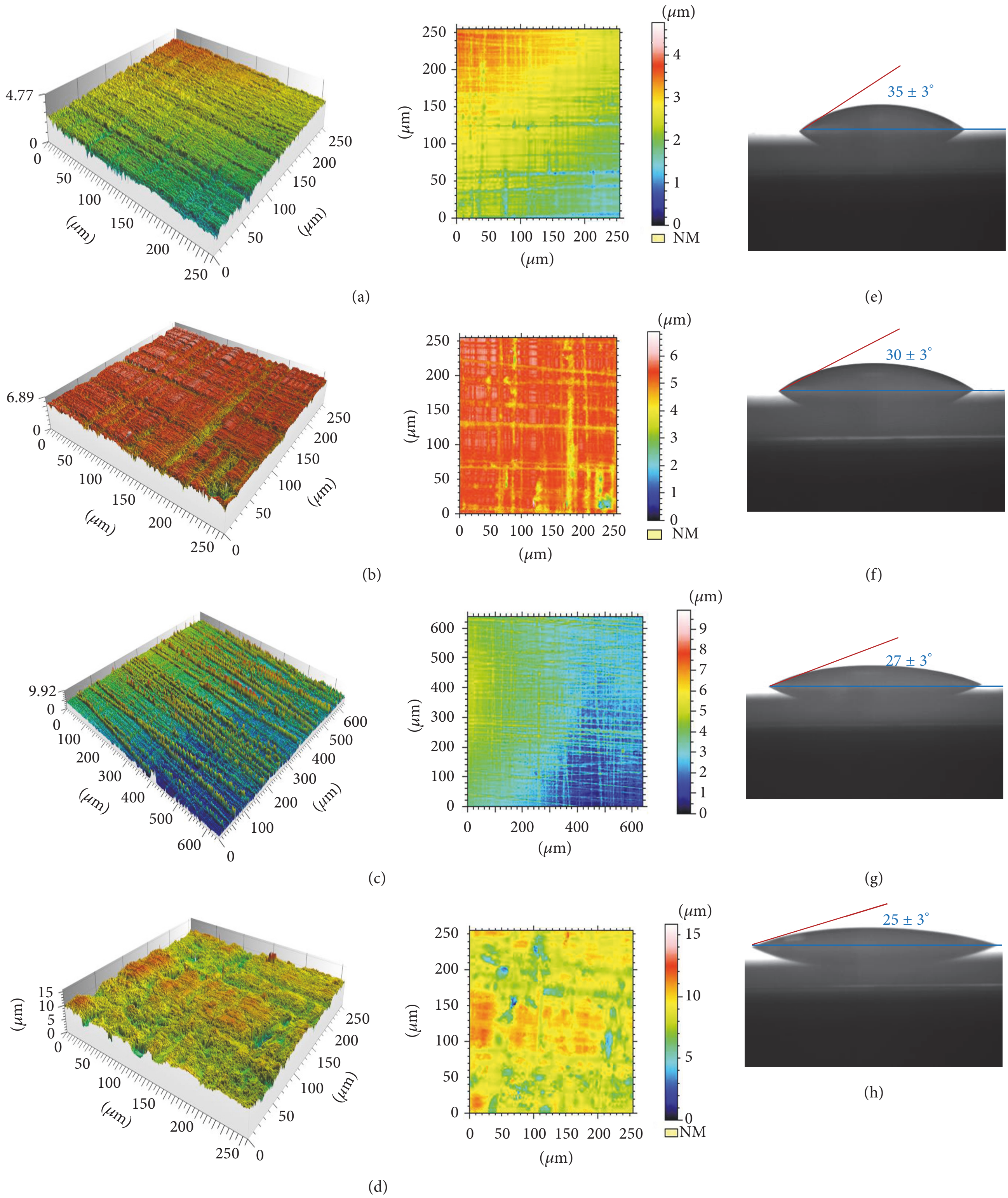

FIGURE 1: Surface roughness and contact angle of PTFE droplets on glass substrates. (a)–(d) Substrates with different roughness, polished using sandpaper with different mesh sizes. Larger sandpaper grain size increased the surface roughness. (e)–(h) Contact angle of the PTFE suspension on the substrate. The contact angle decreased as the substrate become rougher.

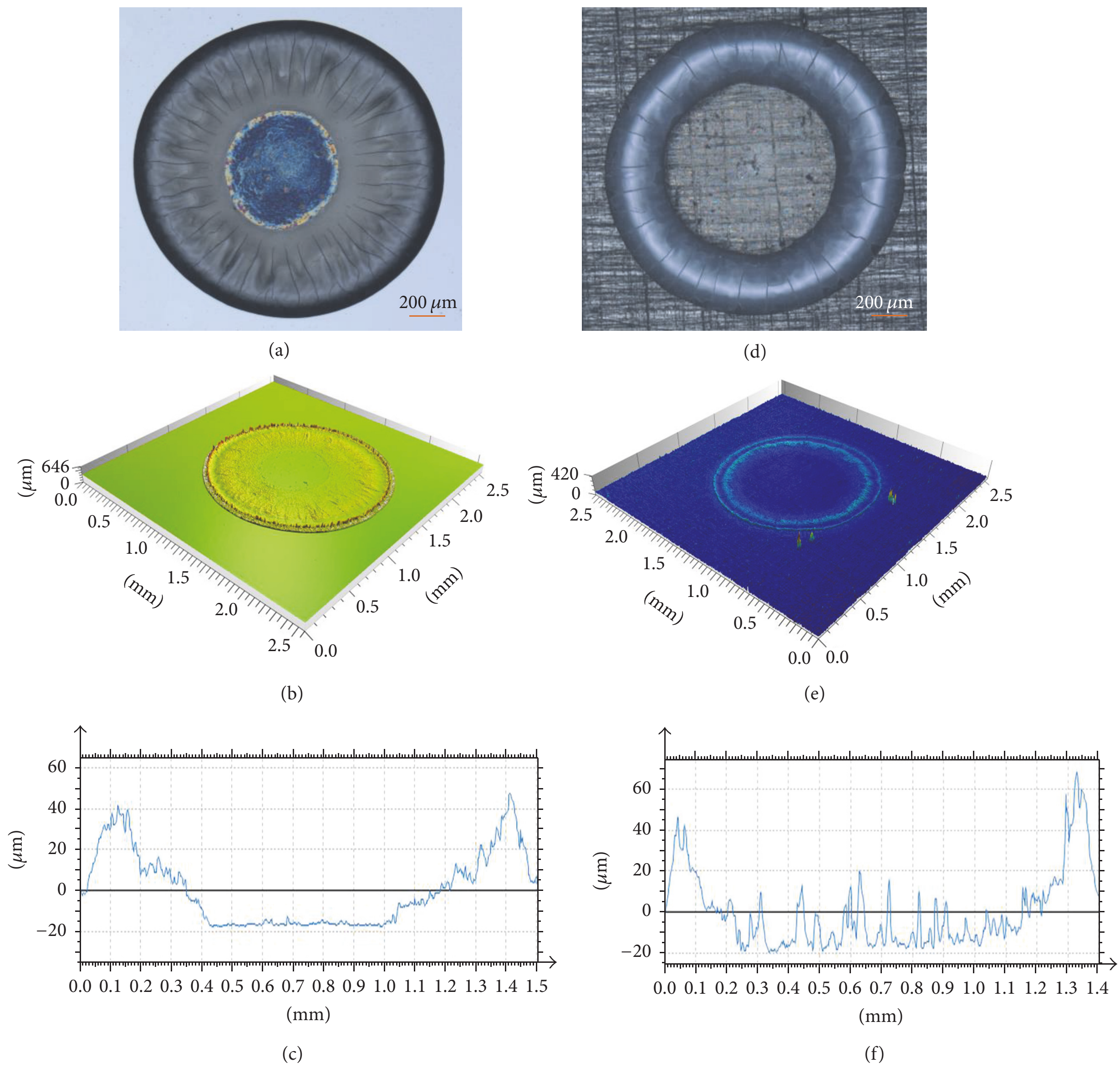

FIGURE 2: Evaporation patterns of PTFE colloidal droplets and their profiles on different substrates: (a)–(c) smooth substrate, (d)–(f) rough substrate.

Figure 3 shows the evaporated patterns of the PTFE droplets deposited on smooth and rough substrates with different roughness. The pattern deposited on smooth glass clearly exhibits the widest coffee-ring. The cross-section is wedge-shaped, as can also been seen in Figures 2(b) and 2(c). With increasing roughness, the width of the coffee-ring decreased. The cross-section gradually changed from wedge- to hill-shaped, which is also exhibited in Figure 2. In addition, with increasing roughness, the total number of the crack decreases while the distance between adjacent cracks increases. The evaporation induced cracking is a competition between elastic energy stored and the surface energy of the newly produced area [16]. With the enhancement of coffee-ring effect due to increasing roughness, the cross-section area of the ring is increased. As a result, the total cracks quantity decreases. Table 1 contains the parameters of the deposited patterns, including the width and height of the coffee-ring, number of cracks, and the distance between adjacent cracks. It should be noted that data listed in the table are average values, obtained at least 10 samples for each parameter.

3.3. Dynamic Process of Colloid Droplets Evaporation. To further reveal the mechanism by which substrate roughness affects pattern formation, we observed the process of droplet evaporation in real time. The evaporation process of PTFE colloid droplets on the smooth substrate is shown in Figure 4. The whole evaporation process lasts about 180 s, during which, cracks nucleate and grow within 3 s. Compared to the

Table 1: Parameters of evaporation patterns on different substrates.

Substrate roughness (mesh of sand paper)	Width of the coffee ring (μm)	Height of the coffee ring (μm)	Crack quantity	Crack distance (μm)
Smooth glass	400 ± 10	55 ± 2	50 ± 5	63 ± 2
1500	250 ± 6	60 ± 2	48 ± 4	65 ± 2
1000	230 ± 5	63 ± 3	46 ± 3	68 ± 2
800	200 ± 5	70 ± 3	45 ± 3	70 ± 2
400	170 ± 4	75 ± 4	43 ± 2	73 ± 2
200	160 ± 4	80 ± 5	40 ± 2	78 ± 2

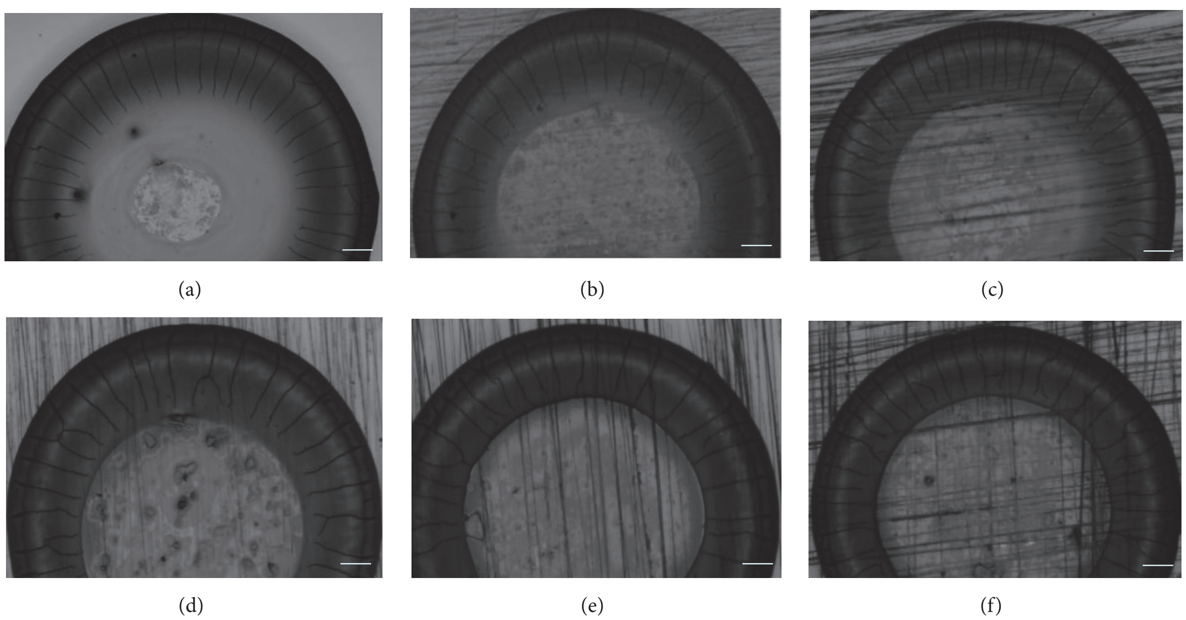

Figure 3: Evaporation patterns of PTFE colloidal droplets on glass slides with different roughness: (a) smooth glass; (b)–(f) increasing surface roughness, achieved using sandpaper with mesh sizes of 1500, 1000, 800, 400, and 200, respectively (scale bars represent 100 μm).

droplet deposited on the rough substrate, the evaporation front of the droplet on the smooth substrate moves more slowly, probably because of the larger contact angle. At the same time, both the capillary flow and Marangoni flow are strong for the droplet on the smooth substrate. The move direction of the flows is reversed, slowing down the motion of the contact line. After formation of coffee-ring, radial cracks emerged. The cracks extend along the radial direction because evaporation of the outer rings causes cracks to be in a tangential tension state.

The evaporation process of PTFE colloidal droplets on a rough substrate is shown in Figure 5. In contrast to the smooth substrate, the whole evaporation process lasted less than 80 s. Crack formation and growth take just 1 s and the contact line moves more quickly than on the smooth surface. After 20 s, radial-shaped wrinkles emerged on the evaporation front. During the later stages of evaporation, the contact line moved more quickly, mainly because of the greatly reduced number of particles remaining in the colloidal suspension. Cracks form cores more easily and grow far more rapidly on the rough substrate than on the smooth one, mainly because the rough substrate offers more nucleation sites, making it easier to form cracking cores. In addition, the thicker coffee-ring stored more energy, enhancing the expansion rate.

3.4. Formation Mechanism of Evaporating Patterns. The evaporation of PTFE colloid droplets is always accompanied by obvious coffee-ring effect on solid substrate (Figure 2), with the contact line of the droplet pinned during evaporation (Figures 4 and 5). As shown by Deegan et al. [5], the capillary compensating flow is caused by the pinning of the contact line and the evaporating heterogeneity of droplets, which also lead to the continuous accumulation of colloid particles at the contact line. Evaporating patterns are always ring-like stains on hydrophilic substrates [10]. However, the deposition morphology is different when the roughness changes. During our experiment, the cross-section changed from wedge- to hill-shaped with the width of the coffee-ring decreasing with increasing surface roughness.

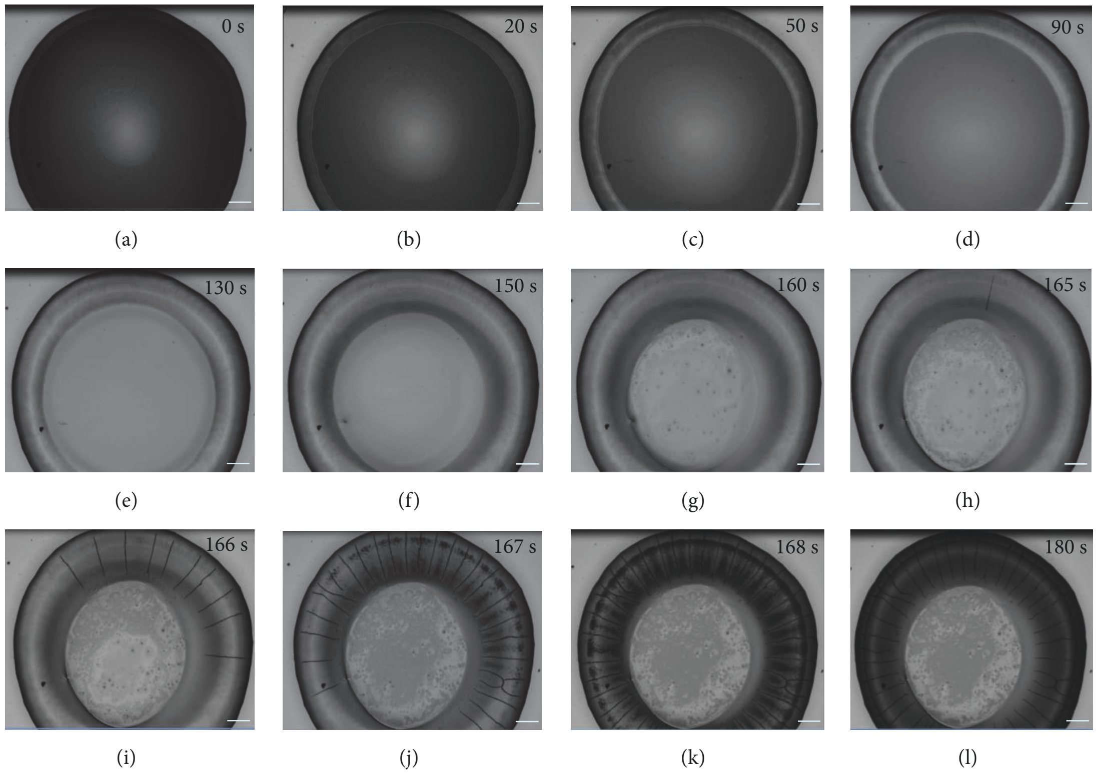

Figure 4: Evaporation dynamics of a PTFE droplet on a smooth substrate. Panels (a)–(l) correspond to different evaporation times (scale bars represent 100 μm).

Several factors contribute to these results, just as shown in Figure 6. The most important is that when the roughness of the substrate increases, the contact angle of the droplet decreases, which leads to an increased evaporation rate at the edges. Meanwhile, the wicking effect provides additional evaporation mass, strengthening the capillary flow. These factors result in many particles moving to the edge. In addition, the roughness of the substrate reinforces pinning of the contact line, intensifying contact angle hysteresis and thus helping particles move to and remain at the edge. In addition, the circumfluence which flows from the edge to the center is hindered by the roughness of the substrate. When the roughness increased to the critical value, the circumfluence along it is hindered, and the capillary compensation circulating current will not be established. Under these conditions, no particles can be brought back to the center. It is worth pointing out that the circumfluence is not hindered when evaporating on smooth substrate, such that it is possible to set up a capillary compensating circulating current. Some particles on the edge, which are transported by the capillary flow, are removed to the center by the circumfluence, resulting in the coffee-ring gradually extending from the edge to the center, as shown in Figure 6(c). Finally, during the evaporation process, helical corrugated wrinkles emerged on the evaporation front, as shown in Figure 5, which also prevent particles located on the edge from moving to the center.

On rough substrates, particles can be easily transported to the edge where they remain. This results in relatively few particles being located in the center after evaporation. The evaporation front moves more quickly during the final stages of evaporation because of the small number of particles in the center. These factors and those described above work together to strengthen the coffee-ring effect, decreasing the width and increasing the thickness of the coffee-ring.

In addition to difference in morphology, the dynamics of crack expansion is influenced by the roughness of the substrate. A greater number of nucleation sites on rougher substrate make crack formation easier. The crack expansion rate on rough substrates is much higher than that on a smooth substrate because the coffee-ring is thicker and stores more elastic energy during evaporation. However, because of the complexity of evaporation and the time variation of crack growth, it is still a great challenge to build a precise dynamic model to describe crack growth during evaporation.

4. Conclusions

We draw conclusions from studying the evaporation and pattern formation of PTFE colloid droplets on smooth and rough substrates:

(1) The coffee-ring effect emerged when PTFE colloid droplets evaporated on a smooth substrate. The cross-section

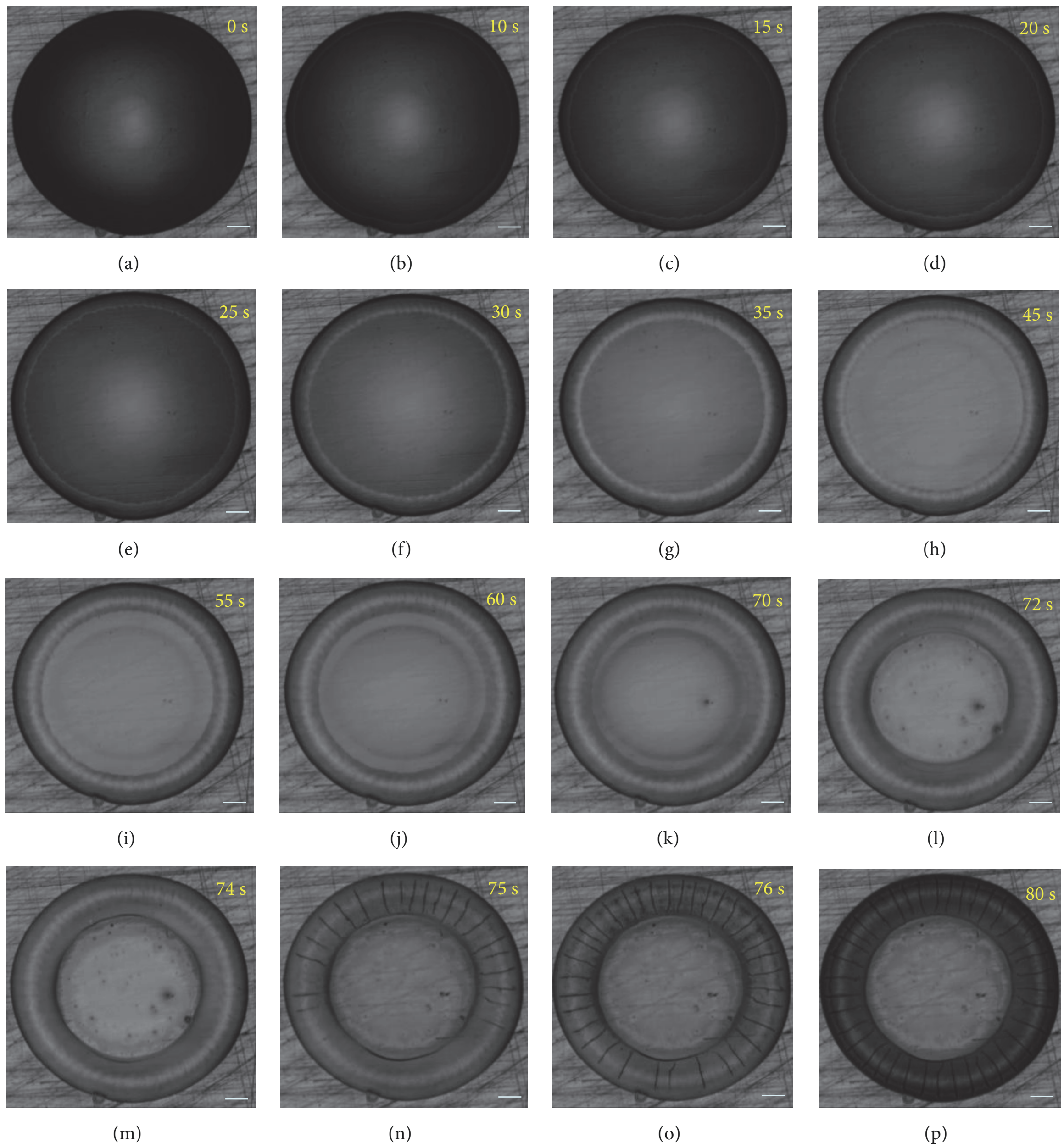

FIGURE 5: Evaporation dynamics of PTFE droplet on rough substrate, (a)–(p) correspond to different evaporation time. The mesh of sand paper used is 200 (scale bars represent 100 μm).

of the deposition was wedge-shaped. Coffee-ring effect was more pronounced when the droplets evaporate on rough substrates. With increasing substrate roughness, the cross-section of the deposition changed from wedge- to hill-shaped.

(2) The evaporation rate of droplets is far higher on rough substrates than on the smooth substrate. This is because of the smaller contact angle on the rough surface and the emergence of the wicking effect which produces additional evaporation mass. These two factors enhance the capillary flow, driving particles to the edge. Meanwhile, the roughness of the substrate helps the pinning of the contact line and increases contact angle hysteresis, which also helps to drive particles to the edge.

In addition, circular flow can not be established on the rough substrate and radial-shaped wrinkle form on the evaporation front, preventing the particles' move to the center. Thus, the rough substrate exhibits a more pronounced coffee-ring effect, with the width decreasing and the height increasing with increasing roughness.

(3) Crack nucleation is easier and the rate of crack expansion is higher for droplet evaporated on rough substrates than on smooth substrates. This is because of the large number of nucleation sites on rough substrates. Because of the thicker coffee-ring, more elastic energy is stored during evaporation, which also enhances the crack expansion rate.

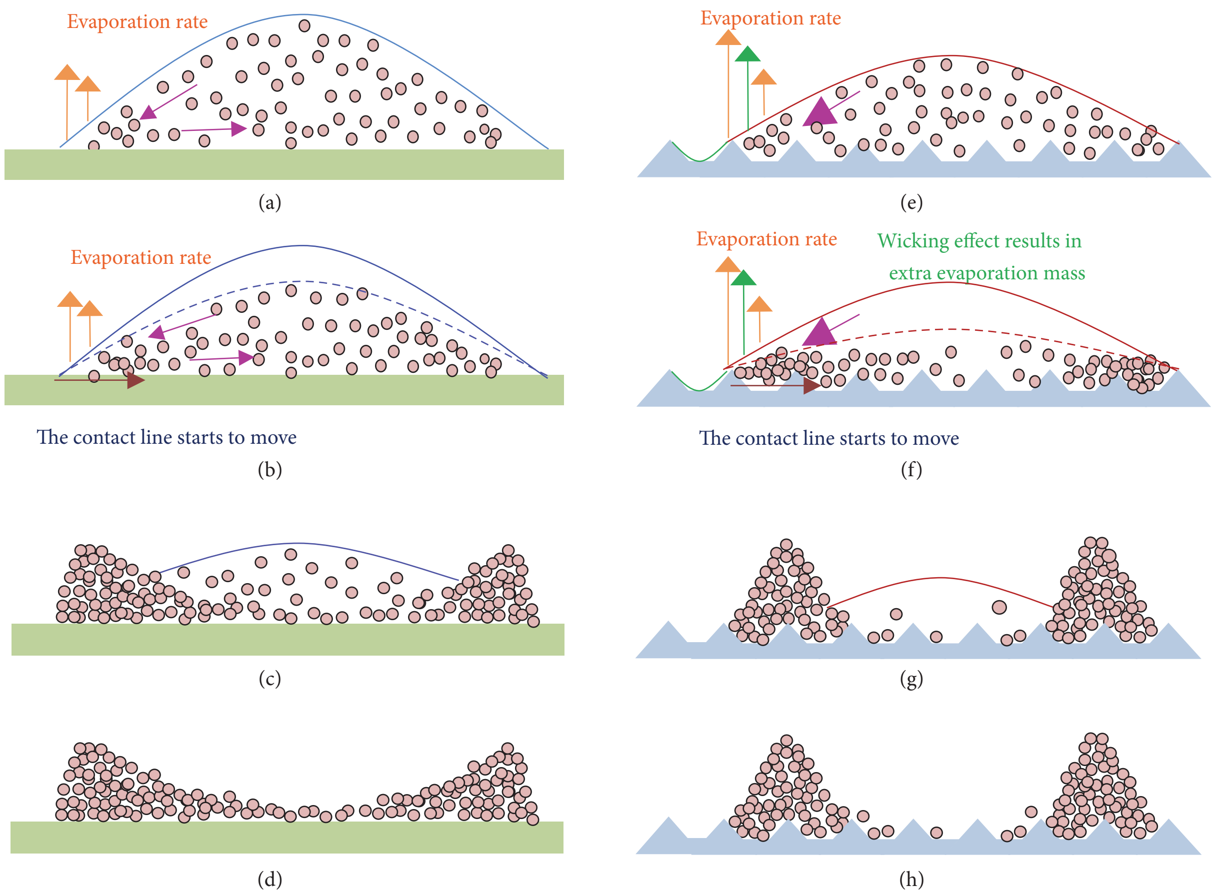

Figure 6: Formation mechanism of evaporation patterns on (a–d) a smooth substrate and (e–h) a rough substrate. (a) On a smooth substrate, the contact angle is larger and the evaporation rate is low; (b) recycling flow is constructed on the smooth substrate; (c) in the later stages of evaporation, many particles remain in the dispersion on the smooth substrate; (d) wedge-shaped cross-section of the deposition; (e) on a rough substrate, the contact angle decreases and the wicking effect emerges, leading to a higher evaporation rate; (f) there is no circumfluence on the rough substrate, with contact angle hysteresis being more evident; (g) almost no particles remain in the center; (h) high-shaped cross-section morphology.

Conflicts of Interest

The authors declare no potential conflicts of interest.

Acknowledgments

This work is supported by the Foundation of Shaanxi Provincial Education Department, China (17JK1123, 16JK2198) and the Xi'an Science and Technology Project (2017CGWL15).

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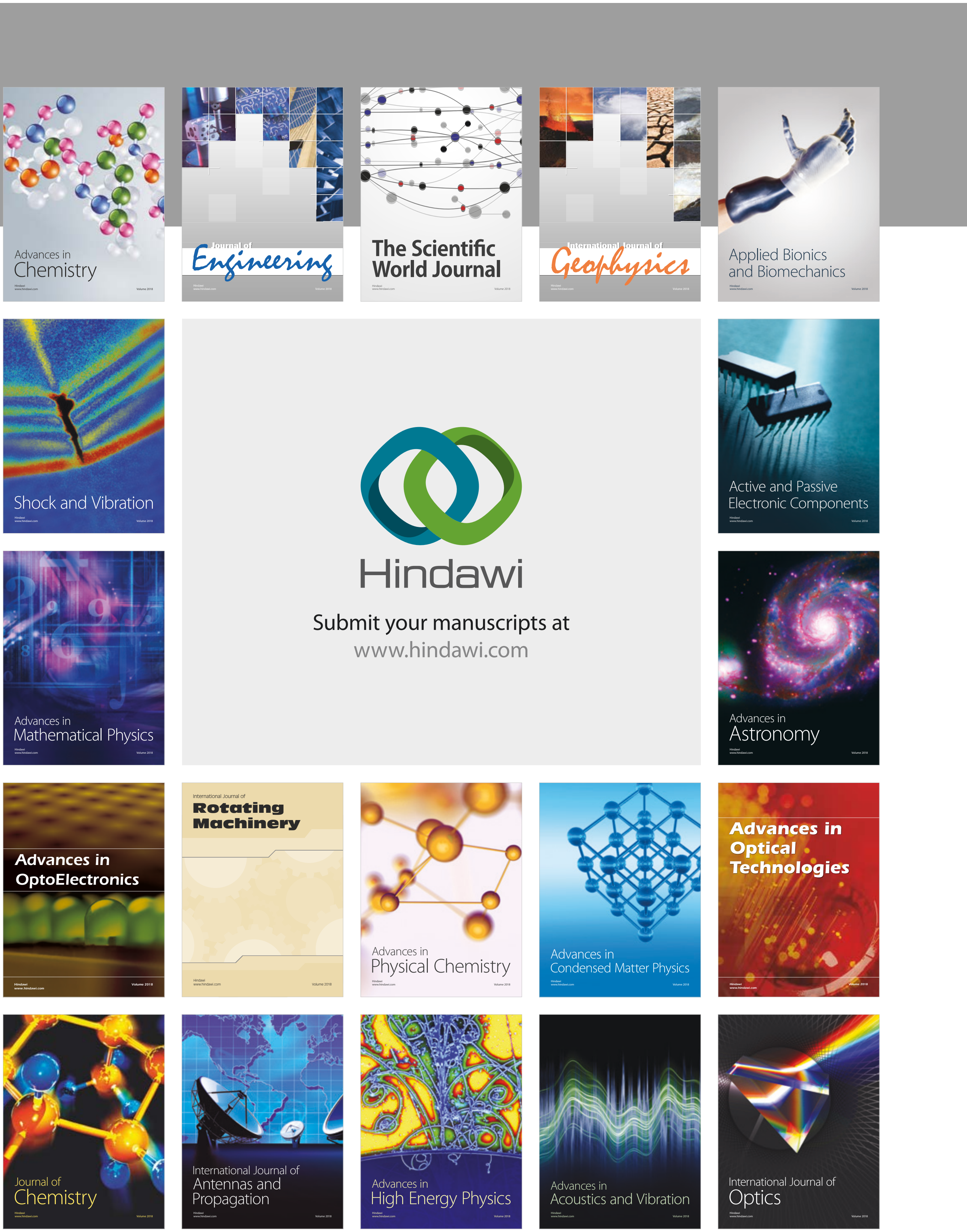

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