Ratchet composite thin film for low-temperature self-propelled Leidenfrost droplet

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ABSTRACT

The droplet control, especially for the self-propelled Leidenfrost droplet, has attracted many researchers' attention in applied and fundamental fields. In this paper, the ratchet thin film was fabricated by magnetron sputtering and hybrid ion beams deposition. The micro- and nanoscale structure of the film was characterized by field emission scanning electron microscope. This study reports an interesting phenomenon that the self-propelled Leidenfrost water droplet was initiated at low temperature. The Leidenfrost point of droplets was controlled by the surface wettability and parameters of the asymmetric ratchet substrate. This novel self-propelled interfacial material and preparation technology can be expanded to the manufacture process and constructed a temperature-dependent tubule for microfluidic systems.

1. Introduction

Microfluidic systems have attracted scientists and technologists in chemistry, biology, engineering and medicine by the enhanced performance characteristics, which are a new series of instrumental platforms to efficiently manipulate process and analyze molecular reactions on the micrometer to nanometer scale [1–3]. The applications in those fields, in return, have an opportunity to stimulate research on microfluidic systems by asking questions that require the development of new capabilities and materials.

Microfluidic systems require improvements on many issues, including droplet control, compatibility with reagents and the removal of side products. The ability to control droplet is a core issue. Methods for manipulating droplets have been developed with progresses in physics and chemistry, for example through hydrodynamics, acoustic waves [4], mechanical vibrations [5], electrokinetics [6,7], thermal gradient effects [8–11], Marangoni effects and surface chemistry [12–16]. Among these methods, a perpendicular thermal gradient system [10] was famous for a self-propelled Leidenfrost droplet that can spontaneously climb against inclines and sustain a speed of 5 cm/s over distances up to 1 m, without any external power. In the development of the perpendicular thermal gradient system, Ok et al. achieved a self-propelled droplet on sub-micron ratchets at a speed of 40 cm/s faster than before [11]. The research of Ok et al. also demonstrated the speculation of Linke et al. [10] that the hydrophobic ratchet surface can decrease the threshold temperature of the droplet motion at nucleate boiling regime. For a Leidenfrost droplet, low hysteresis arises from a lubricating vapor layer separating the droplet from the supporting surface. The fast-motion feature of Leidenfrost droplets makes them attractive for use in millimeter-scale closed loop, two-phase cooling systems with no moving parts or external power, for example microprocessor cooling. If the Leidenfrost droplet is activated at low temperature, the microprocessor will work more safely. In the development of microfabricated systems for use in the chemical and biological science, microfluidic systems based on self-propelled Leidenfrost droplet may be required to satisfy automatic droplet transportation at low temperature for the control and detection of chemical reactions. According to theoretical and experimental studies [17–21], the presence of the surface roughness severely affects the vapor flow field and Leidenfrost temperature in this routine: first, the flow penetrates into the roughness cavities and develops recirculation in each cavity; secondly, the thickness of the vapor layer increases as the size of the droplet relative to the size of the roughness increases; and finally, the thicker the vapor layer is, the higher the Leidenfrost temperature becomes. However, despite intensive research on the relation between surface roughness and heat transfer, there are few reports on the materials for temperature-dependent self-propelled Leidenfrost droplet.

Here, we report a ratchet composite thin film for low-temperature self-propelled Leidenfrost droplet. We tailored the wettability by modifying surface topography and chemistry. The self-propelled droplet can be driven by a thermal gradient perpendicular to the direction of motion on the hierarchical composite hydrogenated carbon surface at a temperature lower than that on the alumina surface. And the self-propelled droplet can be observed to achieve a speed of several centimeters per second on

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these composite hydrogenated carbon films within a distance of 5 mm, which was limited by the resolution of contact angle instrument.

2. Materials and methods

2.1. Ratchet surface preparation

The initial surface was made of a brass square bar (grade 59). It was cut to make five sample surfaces 50 mm long, 25 mm wide and 2 mm thick but with different sawteeth by wire-electrode cutting (Fig. 1, Table 1). These samples were rinsed with wash liquid, which was composed of sulfuric acid (18 mL), 30% hydrogen peroxide (28 mL), ethanol (10 mL) and acetic acid glacial (6 mL). All these regents were analytically pure. After being washed by deionized water, those samples were ultrasonically cleaned in acetone for 10 min and dried by nitrogen flow.

After an aluminum film [22] was deposited on the initial surface with a thickness of about 1 μm by magnetron sputtering (Al 99.99%), ultraviolet radiation was used to make a compact alumina layer on these substrates. To study the wettability of the alumina film, the same film was deposited on slide glass as reference sample. Finally, a composite hydrogenated carbon film [23] with a thickness of about 1 μm was prepared on the alumina layer by a hybrid ion beams deposition system consisting of a magnetron sputtering (Cr 99.99%) and a linear anode-layer ion sources. During film deposition process, hydrocarbon gas (C_2H_2 99.9%) was introduced into the linear ion source to obtain the hydrocarbon ions. A referenced hydrogenated carbon film was also deposited on silicon wafer.

2.2. Surface characterization and water droplet status

Surface morphologies were observed by a field emission scanning electron microscope (FESEM Hitachi S-4800). The droplet dynamic statuses and contact angle measurements were performed with a contact angle instrument (Dataphysics OCA20, Germany). Only deionized water was used in the experiments, and the water was frequently replaced to guarantee fluid properties. A dataphysics TC/TEC 700 was employed to control the temperature of the surfaces. A Chromel–Alumel (K type) thermometer was used to measure the temperature of the top surface (calibrated accuracy ± 2 °C). The droplet with a volume of 4.5 μL was deposited by a Hamilton DS 500/GT precision syringe, and the distance between droplets and hot ratchet surfaces was 5 mm. The changes in the droplet status were recorded by a CCD camera. The contact angle (CA) was collected using water droplets (3 μL) at room temperature (∼ 23 °C). The contact angle data reported here were determined by averaging values measured at five different points on sample surfaces, and the measurement error was in a range of ±2°.
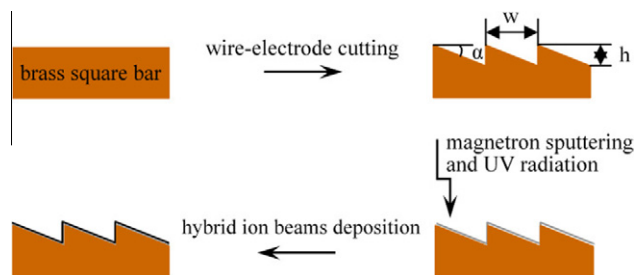

Fig. 1. The schematic fabrication of ratchet composite thin films.

Table 1
Parameters of the ratchet surfaces.

Item	A1	A2	A3	A4	A5
w (mm)	0.75	1.00	1.25	1.50	1.75
h (mm)	0.20	0.20	0.20	0.20	0.20
α (°)	14.9	11.3	9.1	7.6	6.5

3. Results and discussion

The topography of ratchet surfaces is shown in Fig. 2. Fig. 2c and d are the enlarged images of those films; the rough structure of surfaces is characterized by pinecone morphology. The diameters of the pinecone-like particles are in a random distribution, ranging from 100 nm to 3 μm. These results indicate that the prepared ratchet films have a rough surface with both micro- and nanoscale hierarchical structures, which are similar to that of self-cleaning lotus leaf [24].

It is well known that the state of a droplet deposited on a hot surface can be categorized into four regimes [18], namely single phase, nucleate boiling, transition boiling and film boiling regime. As the interface temperature increases, the droplet undergoes the process from the single phase regime to the film boiling regime. When the interface temperature increases further, the bubble increases and forms a continuous vapor layer beneath the droplet. Only the droplet in film boiling regime can surf on the hot surface, due to the lubrication provided by the evaporation film. This droplet took a long time to evaporate at high temperature. When the droplet translated from transition boiling regime to film boiling regime, the surface temperature was termed the Leidenfrost Point (LFP). Fig. 3 shows four typical images of a water droplet on ratchet substrates with different temperature, characterizing droplet statuses at single phase, nucleate boiling, transition boiling and film boiling regime. The experimental results indicated that the LFP of a water droplet on the composite hydrogenated carbon film (133.5 °C) was lower than that on the alumina film (148.1 °C).

As can be seen in Fig. 4, the CA of a water droplet on the A1 film increased due to the micro- and nanoscale hierarchical structures. The results indicated that the hydrophobicity of A1 coated with alumina film was stronger than that coated with composite hydrogenated carbon film. The research of Phan et al. demonstrated that the surface wettability had a significant influence on the heat transfer at nucleate boiling regime [25]. The bubble in contact with the hydrophobic surface did not detach from the substrate and the curvature radius increased with time. At higher heat flux, the bubble spread over the surface and coalesced with bubbles formed at other sites. So the more hydrophobic surface achieved LFP at temperature higher than the less. As shown in Fig. 3, the droplet on A1 coated with alumina film has a larger curvature radius at nucleate boiling regime than coated with composite hydrogenated carbon film. Consistent with the research of Phan et al., the LFP of A1 coated with alumina film was higher than coated with composite hydrogenated carbon film.

Aside from the influence of surface wettability, the surface roughness has significant effects on the Leidenfrost point [17,26,27]. The past researches suggested that a rough surface required a thick vapor layer between the droplet and the surface to sustain film boiling, therefore, possessed a higher Leidenfrost point temperature [26]. Fig. 5 shows the water droplet LFP on the five ratchet alumina surfaces. Compared with the water droplet radius r (about 1 mm), the growth of Leidenfrost droplets on ratchet surfaces can be distinguished in two regions. While the sawtooth width was equal to or less than the water droplet radius, the water droplet LFP increased with the width, for instance A1 and A2. The ratchet surfaces with narrow sawteeth can be good at limiting vapor escape under the droplet. But there was a balance between
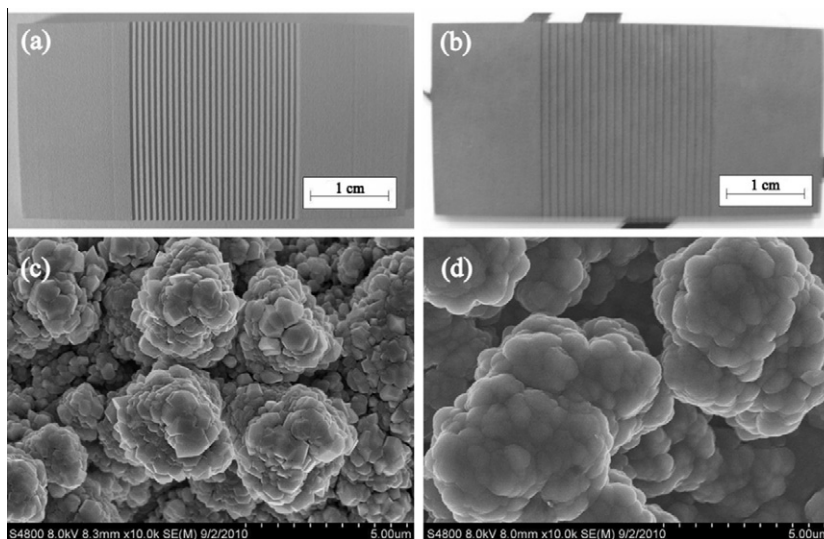
Fig. 2. The topography of ratchet surfaces. (a and b) large-area views of the alumina film and the composite hydrogenated carbon film; (c and d) typical FESEM images of the alumina film and the composite hydrogenated carbon film.
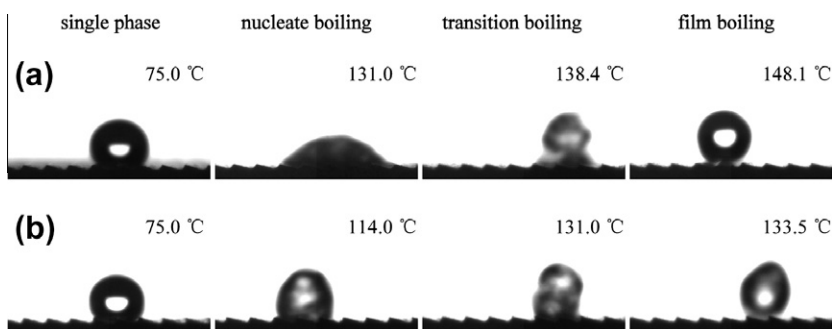

Fig. 3. Typical images of a water droplet on hot substrates. (a) A1 coated with alumina film and (b) A1 coated with composite hydrogenated carbon film. The environmental temperature was 24 °C.
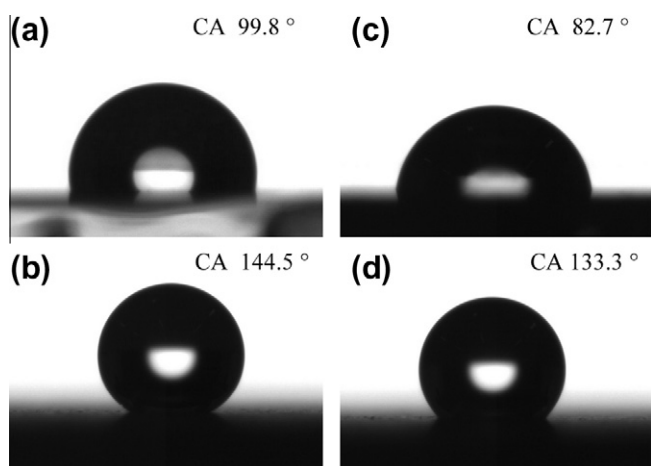

Fig. 4. Photographs of water contact angle on four substrates. (a) a Wenzel droplet on the referenced alumina surface; (b) a Cassie droplet on the A1 surface coated with alumina film; (c) a Wenzel droplet on the referenced hydrogenated carbon surface; (d) a Cassie droplet on the A1 surface coated with composite hydrogenated carbon film.

Fig. 5. The LFP of the water droplet on the five ratchet alumina film (24 °C).

the cage effect and the bubble coalescence. When the cage effect of ratchet surfaces decreased with increase in the sawtooth width, the vapor f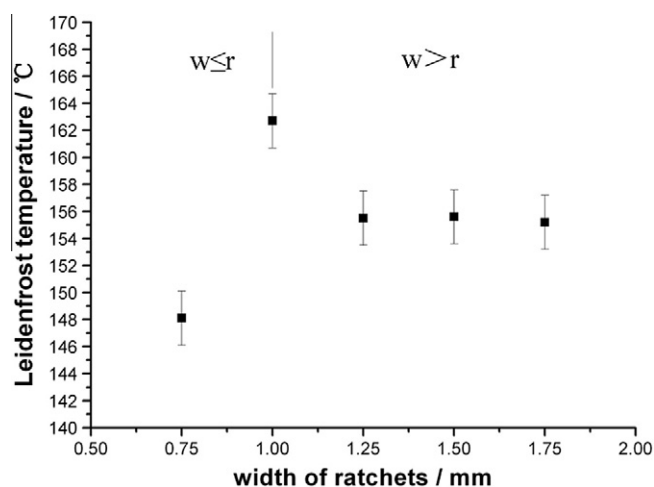ilm stability was disturbed due to the coalescence of the bubbles, and then hindered the coming of the LFP. So A2 ratchet surface achieved the highest LFP. Because the sawtooth width of A3, A4 and A5 surfaces was larger than the water droplet radius, the thin vapor film can be developed on the sawtooth incline. The ribbons of those ratchet surfaces could not cage the water
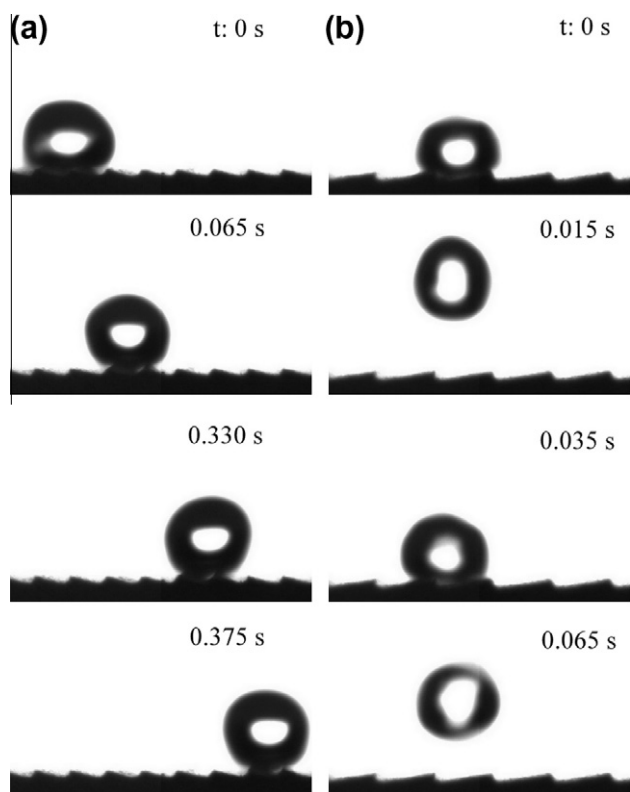
Fig. 6. Dynamic status of Leidenfrost droplets (a and b) for A1 and A3 coated with alumina film.

Fig. 7. The motion curve of the self-propelled droplet on ratchet composite hydrogenated carbon film with different sawteeth.

vapor, and then had a less influence on the LFP. According to the experimental results, it is suggested that the LFP and the dynamic status of water droplets on these ratchet hierarchical alumina surfaces were controlled not only by the surface microstructure but also by the sawtooth parameters.

The results of Linke et al. showed that the self-propelled motion cannot be observed for droplets with radius $r < 0.3w$ on ratchet surface [10]. Contrasted with the Linke's finished samples, our ratchet surfaces had a micro- and nanoscale hierarchical structure; in return, a more violent vapor flow may accumulate under the droplets than the Linke's. So the directive motion on ratchet surfaces with wider sawteeth may be disturbed (cf. Fig. 6b).

A droplet deposited on a hot ratchet surface is nearly spherical while the water droplet radius r is smaller than the capillary length a ($a = (\gamma / \rho g)^{1/2}$ = 2.5 mm, the surface tension γ 58.9mN/m and the density ρ 957 kg/m^3) [28]. As liquid evaporates at the bottom surface of the droplet, a shear force due to Poiseuille vapor flow propels the droplet in forward direction [10]. The droplet trajectory was recorded using a video camera (PULNIX, TM-6740cl, 200 frames per second), and the Dataphysic OCA-20 software was used for tracking the droplet motion. Since the travel distance was only several millimeters (about 5 mm) due to camera view limit, we proposed that the droplet was exerted by a constant force and the velocity was about twice as large as the mean velocity. We fitted the data of droplet position evolution with time with second-order polynomial regression model, and two curves fit well with P < 0.05. The Leidenfrost droplets placed on the ratchet surfaces accelerated against significant inclines, with the effect becoming stronger with decreasing sawtooth width (cf. Fig. 7). On the A1 ratchet composite hydrogenated carbon surface, the millimeter-sized droplets were accelerated to the speed of 3.4 cm/s in 0.19 s (at LFP 133.5 °C). And on the A2 ratchet composite hydrogenated carbon surface, the millimeter-sized droplets were accelerated to
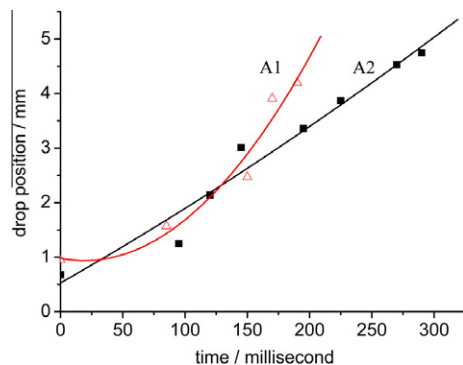
the speed of 2.8 cm/s in 0.29 s (at LFP 150.5 °C). The self-propelled Leidenfrost droplets move more speedily in low-temperature regime, and the Leidenfrost droplet gets a longer life-time at the low-temperature regime than at high-temperature regime [21]. It broadens the application of microfluidic systems for conveying the microdroplets at different temperature.

4. Conclusions

Ratchet composite thin film with designed surface wettability was found to be effective in adjusting the LFP of self-propelled droplets and obtaining low-temperature self-propelled droplets. The more hydrophobic surface may have a higher LFP than the less. And the results demonstrated that the sawtooth width should be smaller than the droplet radius to keep the direction effect strong. Based on this research, we could develop a series of self-propelled interfacial materials to construct a temperature-dependent tubule. The self-propelled Leidenfrost droplets were initiated on the ratchet composite hydrogenated carbon surface at a temperature lower than before, which is suitable for many practical applications. These composite thin films and the preparation technology can be expanded to the microintelligent thermal management system and microfluidic systems.

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