SPONTANEOUS FAST MOTION OF WATER DROPLET ON NANOTEXTURED AND CURVED GLASS SURFACES

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ABSTRACT

This paper reports the study on spontaneous and fast motion for a microliter water droplet on nanotextured glass capillary surfaces with a wide range of curvature gradients. The surface is highly related to the surface tension gradient that is mainly formed by three distinct driving forces, including surface hydrophilicity gradents, chemically patterned nanotexture, and curvature gradient capillaries. In the experiments, the droplet velocity shows a dependency to the droplet position on the conical capillary curvature surface and moves toward the more wettable part of the gradient. The speed of the droplet on the oxygen plasma treated nanotextured glass capillary is up to 238.5 mm/s with more than two times of that, 101.7 mm/s, on the untreated surface. Therefore, we can conclude that a gradual variation of wettability property governs the droplet motion.

KEYWORDS: Droplet motion, surface modification, surface tension gradient, curvature gradient

INTRODUCTION

Self-propelled drops is important due to the disuse of pumps and valves, increasing mixing velocity, minimization of cross-contamination, and dispersionless transport [1]. This technology could become a valuable microfluidic tool in drug screening and DNA analysis [2], and even extended life science application such as quick drainage of condensed liquid drops for fuel cell and semiconductor devices. However, one major challenge in moving discrete liquid droplets is to overcome the hysteresis force and viscous shear force. These two forces will lead to deceleration and stop of the droplet, unless other external forces are applied. Thus, conventionally, spontaneous motion efforts toward the use of surface tension gradient for liquid transport. The most rapid moving speed of the microliter droplet on the plate has been reported up to 500 mm/s in the literature [1]. To further increase this moving tendency, this research incorporates the third driving force: surface curvature gradients [3] for generating ultra high speed and multi-directed droplet movement. The experiments were performed by dispensing a small water droplet (~1 μL) on a conical glass capillary surface with three different surface conditions, including original glass surface, oxygen plasma treated surface, and oxygen plasma treated nanotextured surface. Droplet movement behavior on these three different surfaces were also compared in this study.

THEORY

Considering a droplet moving on a unbalanced interfacial forces between their front and rear end imposed by the unique surface (Fig. 1 (a-c)), conservation of momentum is employed to analyze the dynamics of the droplet moving on the outer of the spherical surface (Fig1.(b)). It can be written as $F = -\partial E / \partial s$, and the developing equation is as follows:

$$-2kE_0 r_0 \left(1-\frac{4}{3}\cdot\frac{1}{\sin^2\theta}\right)\cdot\frac{\partial H}{\partial s} = \rho V_0 \ddot{s}\text{, where } E = E_0\left[1+2kr_0\left(1-\frac{4}{3}\cdot\frac{1}{\sin^2\theta}\right)H\right],\ k = -\frac{4}{3}\cdot\frac{\sin^4\theta}{2-3\cos\theta+\cos^3\theta} \quad (1)$$

Here, the droplet with radius r_0 , volume V_0 , and contact angle θ on a flat surface (Fig1.(a)), ρ is the density of the droplet, E_0 is the surface tension of the droplet such as $E_0 = \gamma(A_{LV} - A_{SL}\cdot\cos\theta)$, γ is surface energy, and A_{LV} and A_{SL} are the liquid –vapor and solid-liquid interfacial surface. Besides, $H = 1/|R|$ is the mean curvature of the spherical surface, R is the radius of the contact area. When a droplet is moving on the inner of the spherical surface (Fig1.(c)), we can also get the same expression of the Eq(1) and $H = -1/|R|$. In the other words, whether H is positive or negative depends on the shape of the contact area. Then we can calculate and integrate the above equation to get the following equation:

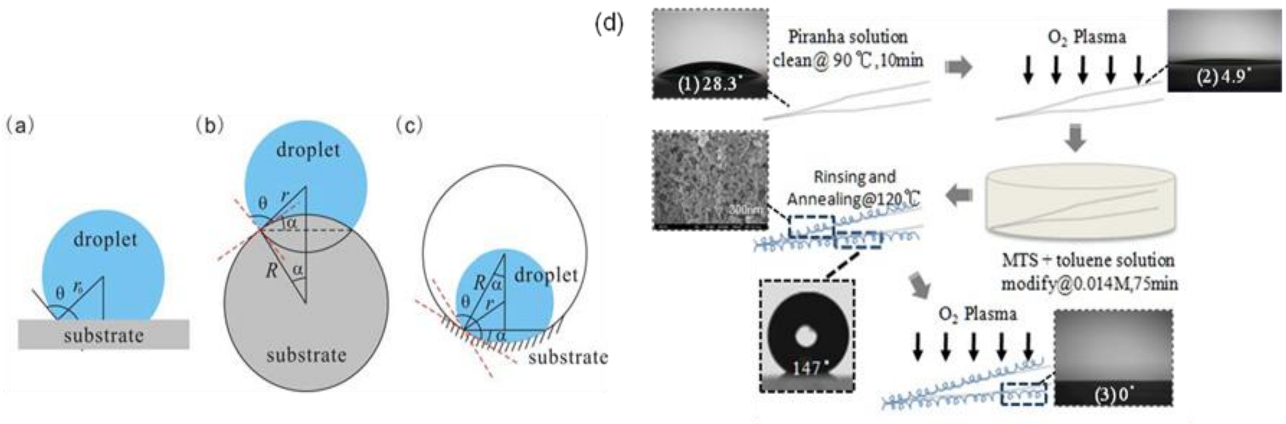
$$\dot{s}^2 = \frac{6\eta\gamma_{LV}}{\rho}\left(\frac{1}{R_0}-\frac{1}{R}\right), \eta = \frac{(1+\cos\theta)(1+3\cos^2\theta)}{2(1-\cos\theta)(2+\cos\theta)} \quad (2)$$

Her, R_0 and R are the initial and the stop local radiuses of the contact area. Moreover, we also need to consider the droplet affected by the hysteresis force and viscous shear force during the movement:

$$\dot{s}^2 = \frac{6\eta\gamma_{LV}}{\rho}\left(\frac{1}{R_0}-\frac{1}{R}\right) - \kappa \cdot \Delta\theta \cdot \frac{\gamma_{LV}}{\rho} s \cdot V_0^{-2/3} - \xi \cdot \frac{\tau}{\rho} \cdot s \cdot V_0^{-1/3}$$

$$\text{Where} \quad \kappa = 4\left[\frac{3}{\pi\left(2-3\cos\theta+\cos^3\theta\right)}\right]^{1/3} \cdot \sin\theta \,,\ \xi = 2\pi\left[\frac{3}{\pi\left(2-3\cos\theta+\cos^3\theta\right)}\right]^{2/3} \cdot \sin^2\theta \qquad (3)$$

Here, $\Delta\theta$ is the contact angle hysteresis, and $\tau = \mu \frac{\partial u}{\partial z}$ is the viscous shear force.



Surface Status	(1) Original	(2) O_2 plasma	(3) MTS $+O_2$ plasma
Contact angle	28.3°±1.14°	4.9°±1.6°	0°

Figure 1. Schematic illustration of a droplet on (a) flat, (b) outer, (c) inner of curved surfaces[3], and (d) fabrication process to form three different statuses on glass capillary surfaces.(Values represent the mean ±maximum/minimum of at least five samples).

EXPERIMENTAL

Figure 1(d) shows the fabrication process to form three different statue surfaces and the contact angles on each surface. The static contact angles (CA) of the original glass and oxygen plasma treated surface are around 28° and 5°, respectively. The chemical patterned nanotextured surface was treated by phase separation of methyltrichlorosilane (CH_3SiCl_3:MTS) [2]. The 3D nanostructures were synthesized by immersing glass capillaries in anhydrous toluene with MTS solution at a concentration of 0.014 M for 75 mins under 23 ℃ and 75 %RH environmental condition. After the treatment, the nanotexture provides the superhydrophobic surface with a static contact angle (CA) and hysteresis of about 147° and 10°, respectively. The surface was then treated by oxygen plasma to decrease the contact angle to about 0° on the nanotextured surface. Three different surface conditions, including original surface, O_2 plasma treated one, and O_2 plasma treated MTS-modified glass capillaries will be compared their droplet moving velocity herein.

RESULTS AND DISCUSSION

In all cases, water droplets can be self-directed and transported toward the capillary's larger cross-section region (with lower curvature). The fastest velocity always occurs on the surface with the largest curvature gradient. The evolution of droplets movement are shown from Fig2.(a-g) representing droplet moving process on original (CA= 28°), O_2 plasma treated (CA=5°), and MTS with O_2 plasma treated (CA= 0°) capillary surfaces, respectively. Furthermore, droplets deposit on these three different kinds of curvature gradients were compared in this study, and the radius of curvature gradients are selected to 0.3–1 mm, 0.3–1.5 mm, and 0.1–1 mm. The 1-μL droplet cannot move on the two former sizes on the original and oxygen plasma treated surfaces, the droplet just wetting the surfaces. However, the droplet moving speed on the smallest size capillary (0.1–1mm) can approach a maximum of 101.7 mm/s, 174.2 mm/s and 238.6 mm/s for original, O_2 plasma treated ,and MTS treated capillary surfaces, respectively, as shown in Fig2.(h-i). In the same figure, droplet occupies larger curvature gradients also carry out a higher moving velocity. The droplet always move starting from the region with the smallest radius (the largest curvature) and stop at the area without curvature gradient. In other words, the droplet velocity along the trajectory presents an accelerating speed at first and then gradually reduces the speed to the zero.

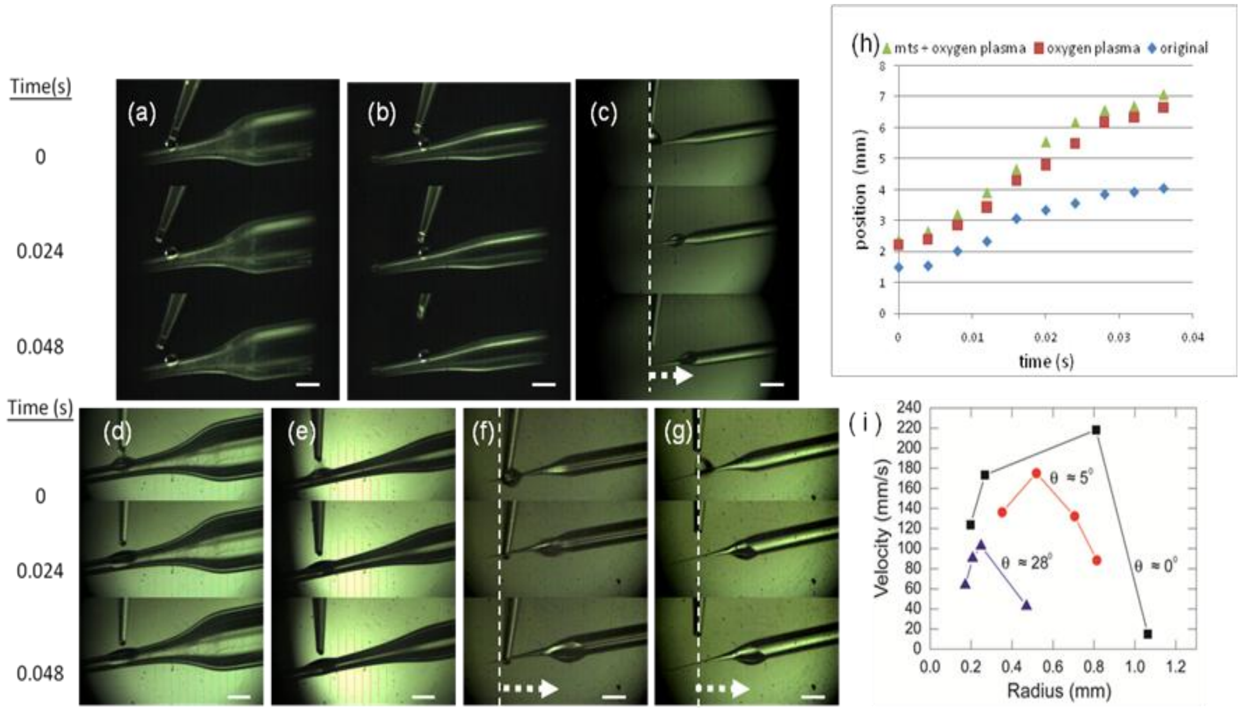


Figure 2. Self-motion behavior of a 1 μL water droplet occupying different curvature ranges (a, d) 0.3–1 mm,(b, e) 0.3–1.5 mm, (c, f, g) 0.1-1 mm. (where (a-c) are original surface, (d-f) are O_2 plasma treated surface, (g) is MTS nanotexture and O_2 plasma modified surface) (scale bar: 2 mm), (h) position evolution of 1 μL droplet movement on the 0.1-1 mm surface under different conditions, and (i)the relationship of velocity and radius of a droplet moving on 0.1-1 mm radius gradient glass capillary.

CONCLUSION

In summary, we have applied the curvature gradient conical capillary surface to facilitate the microliter droplet spontaneous fast motion on the hydrophilic surfaces. The droplet profile and velocity are related to the surface hydrophilicity (CA) and the capillary size (curvature). For a water droplet, the fastest speed is established on the superhydrophilic and the smallest size surface (largest curvature). The intrinsic behavior of the droplet could be concluded and predicted by using submicroliter droplet moving on a capillary with smaller than 0.1 mm diameter size to obtain ultra high speed droplet movement. The finding is potentially useful for manipulating water droplet of micro-nano-liter and could be a valuable microfluidics tool for the applications in drug discovery, even for life science such as fuel cell and semiconductor devices.

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