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Soft elastic superhydrophobic cotton: A new material for contact time reduction in droplet bouncing

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ABSTRACT

Reducing the contact time while water droplets impact on solid surface has become a vital object concerned by many researchers in recent years. However, previous methods of preparing superhydrophobic surfaces for shortening the contact time, with low efficiency and high expense, are not suitable for large-area fabrication and some obtained surfaces cannot work unless droplets just impact on the specific textures which limits their application in the field of anti-icing from freezing rain. Moreover, the contact time reduction has been mostly observed on metals, but rarely on nonmetals. Here, a facile method of fabricating superhydrophobic cotton was first conducted to largely reduce the contact time between droplet and substrate surface, which obviously eliminated the previous weakness. The treated cotton showed an excellent self-cleaning property and water droplet could also easily roll off the surface. The subsequent impact experiments show that the contact time was shortened by ~ 36% compared with that on the regular hard superhydrophobic surface. Moreover, the influence of the impact velocity and droplet radius on the overall contact time or spreading time and recoiling time had been also observed. And the elasticity of soft elastic superhydrophobic material plays a significant role in making the droplet early bounce off the surface causing a large contact time reduction, which leads to a new way to understand the dynamics of bouncing droplets.

1. Introduction

Droplet bouncing behaviors have drawn much attention from scientists and scholars in the last decades, and the dynamics of water impacting on solid surface are of great importance in many industrial applications consisting of staying dry [1–3], anti-icing [4–7], spray cooling [8,9], self-cleaning [10–14], pesticide delivery [15,16], and inkjet printing [17,18]. Especially on a superhydrophobic surface with rough textures, the impinging water droplet was observed to bounce off the surface after a short contact time which was depending on the droplet radius, impact velocity, surface morphologies, surface temperature, and surface-liquid interactions [19–24]. Recent researches have shown that by creating macroscale textures on a water-repellent substrate, including big pyramidal posts [23,25], nickel wires [26], and submillimetre ridges [1,27], there is a remarkable short of the contact time to some extent when droplet rebound from the surface [1,23,25–27]. Liu et al. [23] fabricated the superhydrophobic copper surface patterned with a square lattice of tapered posts, and successfully made water droplet easily bounce off the surface in a pancake shape with a contact time reduction of ~80%. Bird et al. [1] obtained macrotextured laser-ablated ridge silicon surface and ridge-milling metal surfaces, finally revealed the result that the impinging droplet split into small ones and the overall contact time was reduced by ~37%. Gauthier et al. [26] deposited the nickel wires on the hole-drilled Al surface and subsequently spray painting to make it superhydrophobic, the final impact experiments demonstrated that there was a step-like variation of the contact time with impact velocity which was reduced by ~ 44% compared with that on regular superhydrophobic surface. Shen and coworkers [27] constructed some complex ridge macrotextures by CNC milling on micro-nanoscale hierarchical structured superhydrophobic surface, and the subsequent impact experiments revealed that the overall contact time was reduced by ~ 53% to 5.5 ms. Despite an extremely short contact between droplet and solid surfaces, low efficiency and high expense of fabricating these surfaces have become relatively common problems which limit their further applications.

However, reducing by a large amount of the contact time when droplet impacts on nonmetals with excellent superhydrophobicity has rarely been reported before. Just in 2016, Weisensee et al. [24]

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observed the bouncing behaviors of droplet impacting on elastic superhydrophobic polymer (polymethylmethacrylat, PMMA) surface prepared by spraying and just obtained a two-fold reduction in contact time. Lately, Song et al. [28] realized the typical pancake bouncing with ~58% reduction in contact time on the superhydrophobic polymer (shape memory polymer, SMP) pillar arrays fabricated by a replication-spraying method, which was suitable for large-area fabrication.

In general, the methods of preparing these surfaces are not suitable for either large-area fabrication, or anti-icing from freezing rain application because freezing rain droplets cannot just impact on these specific textures (ridges). But for soft elastic materials, once the superhydrophobicity is obtained, it will be extremely simple to realize the large-area fabrication and well applied in fields of anti-icing from freezing rain since the soft elastic substrates will accelerate droplet's jumping wherever freezing rain droplets impacted. In 2014, Lu et al. [29] first showed that water bouncing could be used to identify superhydrophobicity for the superhydrophobic soft porous materials prepared by a generic two-step method. However, change of contact time between water droplets and substrates was not further explored. Here, a facile method of preparing superhydrophobic cotton (a kind of soft elastic superhydrophobic material), including fluorination and coating of particles, is conducted for the purpose of largely reducing the contact time of a rebounding droplet. Especially, where water droplet falls on this soft elastic superhydrophobic material, there is an elastic bending deformation which can help to shorten the contact between droplet and surface to some extent. And the final results show that this approach allows us to shorten the overall contact time by ~36% compared with that on regular flat surfaces. More importantly, we investigate how this reduction varies with impact velocity and droplet radius, which leads to a new way to understand the bouncing dynamics on the soft elastic superhydrophobic surface.

2. Experimental section

2.1. Materials

Cotton was purchased from Dalian Shanping Medical Co. (China). Titanium oxide (TiO_2; anatase) nanoparticles (40 nm in diameter) and fluoroalkylsilane [FAS, $C_8F_{13}H_4Si(OCH_2CH_3)_3$] were purchased from Sigma-Aldrich (USA). Commercially available aluminum (Al) plates (2 mm thick; purity > 99%) were purchased from the Dalian Aluminum Material Manufacturer (China). The rest of the chemical reagents used in this experiment were of the highest possible grade and purchased from Tianjin Kermel Chemical Reagent Co. (China). In the experiment, deionized water (surface tension $\gamma = 72$ mN/m, density $\rho = 1000$ kg/m^3) having different droplet radius were taken to impact superhydrophobic surfaces. In addition, water was also dyed red to strengthen the visualization which almost did not change the surface tension of the droplet.

2.2. Preparation of the superhydrophobic cotton

A simple fluorination and coating of particles were used to fabricate the superhydrophobic cotton as schematically in Fig. 1(a). Prior to modifying cotton, 12 g TiO_2 nanoparticles was placed into 50 g of the 1 wt% ethanol solution of FAS and well mixed for 30 min immersion time. The particles attachment was then conducted. We put the original cotton into the mixture, and it was mechanically stirred for 2 min at 500 rpm to make a paint-like suspension. Finally, the treated cotton was taken out and subsequently maintained at 100 °C for 30 min before testing. In comparison with soft elastic cotton, superhydrophobic Al surfaces were subsequently prepared which were regarded as hard superhydrophobic surfaces. The polished flat Al plates were electrochemically etched in the 0.1 mol/L NaCl electrolyte at 500 mA/cm^2 processing current density for 6 min to obtain micro-scaled structures. After that, the Al plates were rinsed with deionized water and then immersed into boiling water for 40 min to get nano-scaled rough structures. Then, the Al plates were immersed into a 1.0 wt% ethanol solution of FAS for 40 min and subsequently heated at 100 °C for 20 min.

2.3. Characterizations

The surface morphologies of the obtained samples were characterized using a scanning electron microscope (SEM, SUPRA 55 SAPPHIRE, Germany). The chemical compositions were observed by an X-ray diffraction meter system (XRD, Empyrean, Holland) and a senior Fourier transform infrared spectrophotometer (FTIR, Thermo Fisher 6700, USA). The apparent contact angle (CA) of water drops on the as-prepared samples were measured with an optical contact angle meter (SL200KS, KINO, USA) at room temperature.

2.4. Impact experiments

The whole impact experiments were conducted at room temperature with 55% relative humidity. Water droplets with different volumes were generated from different needles equipped with a syringe pump (Longer Pump, LSP01-1A) at different heights, which enabled a variation of the radius (R) of the droplets between 0.993 and 1.711 mm (corresponding to volume 4.1 and 21.0 μL). By adjusting the height which droplets fell, the impact velocity (v) could be varied between 0.447 and 1.549 m/s (corresponding to height 1 and 12 cm). For each needle, the droplet size was obtained by weighing ten drops on a precision balance and subsequent calculating. In addition, the dynamic bouncing processes of water droplets on the superhydrophobic cotton were recorded by a high speed camera (Hot Shot 512 SC camera equipped with a Nikon 105 mm f/2.8 G lens) at the rate of 8000 frames per second from NAC Image Technology Inc. (USA).

3. Results and discussion

3.1. Bouncing dynamics

Fluorination and coating of particles are both important to make cotton superhydrophobic. Fig. 1(b) and (c) show the surface morphology of the fabricated superhydrophobic Al surface and treated cotton. Hard Al substrate was covered with micro-scaled step-like structures and nano-scaled need-like structures after electrochemical etching and boiling-water immersion (Fig. 1(b)). The intrinsic water CA on the prepared hard Al surface was measured to be 165.5° ± 2.3°, and the contact angle hysteresis on the surface was measured to be < 5°, showing an excellent superhydrophobicity. By contrast, the treated cotton had the crisscrossed structures comprising of many cotton fabric rods with single diameter of ~10 μm at the low magnification (Fig. 1(c)). Obviously at the large magnification, superhydrophobic cotton fabric rods were rough and covered with nano-scaled particles after coating of particles and subsequent heat treatment. The inset optical image shows that, although there were no easily observable contact line between water droplet and cotton surface, water droplet was close to a perfect sphere on samples illustrating that samples had the superhydrophobicity. Meanwhile, water droplets could easily roll off the treated cotton surface without any residuals and the treated cotton did not get dyed red after immersed into red dyed water, demonstrating the excellent self-cleaning properties (see Video S1). As shown in Fig. 1(d), the XRD pattern was used to analyze the crystal structures of the treated cotton. Compared with pattern of the untreated cotton, there were eight strong diffraction peaks of Titanium Oxide (JCPDS 01–0562) from the treated cotton, showing the expected patterns for TiO_2 nanoparticles. Fig. 1(e) shows the FTIR spectra of the untreated cotton and treated cotton. Two absorption bands at around 1232 and 1145 cm^{-1} were assigned to the C–F stretching vibration of the $–CF_2–$ and $–CF_3$ groups of the FAS molecules. Hence, the FTIR