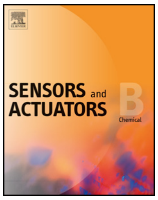
Sensors and Actuators B 262 (2018) 595–602

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb



Developing a non-optical platform for impact dynamics analysis on nanostructured superhydrophobic surfaces using a quartz crystal microbalance

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ARTICLE INFO

Article history:
Received 14 November 2017
Received in revised form 29 January 2018
Accepted 2 February 2018
Available online 7 February 2018

Keywords:
Superhydrophobic
Quartz crystal microbalance
Impact dynamics
Water-repellency
Zinc-oxide nanowires

ABSTRACT

Quantitative analysis of water droplet behavior under dynamic conditions is one of the critical challenges for applications of wettability-controlled surfaces. Currently, various optical analysis techniques have been employed to analyze impact dynamics. Despite the convenience of direct observation of water droplets, most of these techniques have limited applicability to microscopic and quantitative investigations. In an effort to overcome these limitations, here, we suggest a complementary analysis platform using a quartz crystal microbalance (QCM) to study impact dynamics. A high-speed camera and QCM were applied together to study the behavior of water droplets that impact wettability-controlled surfaces with various *We* numbers (Weber number). For these experiments, ZnO nanowire surfaces were prepared and chemically modified by alkyl-thiol molecules with various carbon chain lengths (C0–C12) to control the surface energy. For nanowire surfaces with high surface energies (C0–C6) and for the lowest surface energy sample (C18), both methods exhibited highly consistent impact dynamics, showing stable wetting and dewetting properties, respectively. In addition to these apparent behaviors, QCM was further able to provide detailed microscopic information regarding the penetration and deformation of water droplets in a quantitative way based on acoustic sensing. More interestingly, QCM was able to determine the metastable water repellency of a C12-modified surface with a high *We* number, which could not be detected by the high-speed camera. These results suggest the significant potential of QCM as a new platform to analyze the impact dynamics of water droplets *via* quantitative, microscopic investigations.

1. Introduction

Since superhydrophobic surfaces were first reported several decades ago, numerous studies have been performed on the fabrication and application of these non-wetting surfaces [1–9]. According to the Cassie-Baxter model, a superhydrophobic surface that bio-mimics the lotus leaf exhibits outstanding water-repellency due to the plentiful air pockets provided by the micro/nanostructures [10]. By virtue of this property, this material has been introduced for various applications, such as self-cleaning surfaces, water harvesting, anti-fouling, waterproof devices and medical use [11–16]. In these practical applications, the superhydrophobic surfaces should maintain their non-wetting properties stably under dynamic rather than stationery conditions. Various efforts have been made to investigate and improve the stability of the superhydrophobic state under practical conditions, including colliding droplets, hydraulic pressure, fluid drag as well as severe temperature or pressure [17–21].

Among these controlling parameters, water droplet collision is one of the most important factors because superhydrophobic surfaces experience stability issues, not only in outdoor applications, such as self-cleaning windows, but also in industrial applications, such as inkjet printing and spray coating. Compared with the static condition, the kinetic energy transfer from the impacting water droplets to the surface during the collision causes deformation of the water droplet itself and of the air pocket among micro/nano-structures, thereby strongly affecting the stability of the non-wetting state. Other important parameters that determine the dynamic behavior of impacting water droplets include

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https://doi.org/10.1016/j.snb.2018.02.031
0925-4005/

surface energy and the microstructures where the water droplets collide. Many studies have been performed to understand the interplay among these parameters in determining the dynamic impact behavior of water droplets and the stability of the non-wetting state [22–27].

Most studies of impact dynamics have used optical analysis tools, such as a high-speed camera, fluorescent microscopy, and x-ray phase-contrast imaging [28–35]. These techniques enable real time observation of impact dynamics by immediate observation of the changes that occur at the surface due to impacting water droplets. Although observation with optical methods provides intuitive information on the behavior of the water droplet during impact dynamics, these methods are limited in the direct tracking changes at a surface, observable dimension and ability to provide quantitative data. Thus, it is necessary to develop a non-optical platform to enable direct, quantitative investigations of impact dynamics. We applied QCM (quartz crystal microbalance) as a complementary tool for optical analysis, in particular for impact dynamic studies coupled with a high-speed camera. This technique can be used to investigate *in-situ* changes of the surface state (*i.e.*, adsorption mass and surface stress) by using quantitative values, including the resonance frequency and dissipation factor.

In the present study, the impact dynamics of water droplets were first analyzed by a conventional high-speed camera, and the results were compared with quantitatively analyzed QCM data. For these experiments, the QCM surfaces were modified by thiol-modified ZnO nanowires, which showed different wettability depending on the coating molecules, and then, the variations in the resonance frequency were monitored upon impact. QCM was able to directly detect small water residues by observing microscopic changes on the surface, even if those changes were too small to be observed by a high-speed camera. The stability of the water-repellency of superhydrophobic surfaces as well as the penetration depth determined based on the surface energy were compared based on quantitative analysis using QCM. Complementary observation using QCM can contribute to overcoming the weaknesses of optical methods by providing quantitative, sensitive observations for studies of the droplet-surface behavior, such as evaporation, wetting state transition, condensation-induced droplet jumping, and impact dynamics.

2. Experimental

2.1. Materials

All of the chemicals used in this study were purchased from Sigma-Aldrich (Saint Louis, MO), including zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%), ammonium hydroxide (28 wt%, NH_3 in water), and alkyl-thiols (1-hexanethiol, 1-dodecanethiol, 1-octadecanethiol; HT, DT, ODT). The quartz crystals (5 MHz) were purchased from Stanford Research Systems (Sunnvale, USA). The high-speed camera was manufactured by Photron (Fastcam SA4).

2.2. Growth of ZnO nanowires on QCM and surface modification

ZnO nanowires were grown directly on the QCM and conveniently synthesized using the hydrothermal method [36,37]. Before growing the ZnO nanowire, the 30 nm ZnO seed layer was deposited on the QCM surface by sputtering for 5 min. Then, the QCM samples were dipped in a solution of 10 mM zinc nitrate hexahydrate, and 3 ml of ammonium hydroxide was added to the zinc nitrate hexahydrate solution. The solution including the QCM sample was maintained in a 95 °C oven for 2 h. The QCM samples were washed with distilled water and dried by nitrogen gas. After growing the ZnO nanowire, the samples were coated with a SAM (self-assembled monolayer) to reduce the surface energy [38]. In this study, we used a thiol solution as the SAM material. Alkyl thiols with different carbon chain lengths from 6 to 12 were dissolved in ethanol at a fixed concentration of 10 mM. The ZnO grown QCM samples were immersed in solution for 1 h. Then, the samples were washed with ethanol and dried by nitrogen gas.

2.3. Wettability measurements of ZnO nanowires

The contact angle and contact angle hysteresis of each sample were measured using a SmartDrop analyzer (Femtofab, Korea). To improve the measurement accuracy, the contact angles were measured at three different positions on each sample as a 10 μl water droplet was mounted on. The contact angle hysteresis of each sample was measured by the captive method. The droplet volume was adjusted through a nozzle after a 10 μl water droplet was placed on each sample. When the contact area began to widen as the volume of the water droplet increased, the contact angle was measured to obtain the advancing angle. By contrast, when the contact area began to decrease as the volume decreased, the contact angle was also measured to obtain the receding angle. Finally, the contact angle hysteresis of each sample was calculated by simply subtracting the receding angle from the advancing angle. The sliding angle was obtained by the tilting method. The sample-mounted stage was tilted continuously while the SmartDrop system traced the water droplet. When the water droplet started to move, the sliding angle was determined.

2.4. Measurements with the high-speed camera

First, a high-speed camera was introduced to observe the behavior of impacting water droplets. The water droplets were dropped to the desired spot on the sample through a free fall, and the volume of the droplets was uniformly adjusted using a precision nozzle and syringe pump (10.46 ± 0.36 μl, n = 50). The frame rate of the high-speed camera was maintained at 4500, and the resolution was 896 × 640 at 4× magnification. As the water droplet was transformed during impact, the pictures are organized from the moment of impact to the time that the droplet bounced.

2.5. QCM analysis of impact dynamics

The changes in the resonance frequencies of the quartz crystal samples were monitored *in situ* using a QCM200 (Stanford Research Systems, USA). The QCM sample was placed in a quartz holder and connected to the oscillator and counter unit of the QCM200 to obtain the resonance frequency. The gate time of data acquisition was fixed as 1 s, and the average value during each acquisition was obtained as the resonance frequency. Repeated experiments confirmed that the collision could be tracked using the QCM200, even though the collision process lasted several tens of milliseconds (See Fig. S1). Water droplets were dropped onto the samples using the same method as described above. The water that bounced off the collided surface was immediately removed with an absorbent pad.

3. Results and discussion

3.1. Synthesis of ZnO nanowires and surface modification

In this study, we prepared ZnO nanowires grown on a QCM surface and then modified the nanowires by chemical modification using self-assembled monolayer (SAM) coatings. Fig. 1a presents a schematic diagram of the fabrication process of the ZnO nanowires on the QCM surface. The ZnO seed layer was first deposited on the QCM surface by magnetron sputtering, and then, ZnO nanowires