



Making sponge breathe: A smart way to realize long durability superhydrophobicity



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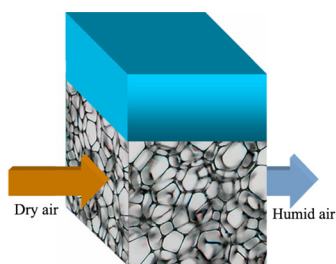
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HIGHLIGHTS

- Superhydrophobic sponge is prepared by grafting the hydrophobic moiety.
- Global sponge superhydrophobicity can be theoretically interpreted.
- Aeration can elongate superhydrophobicity durability in underwater environment.

GRAPHICAL ABSTRACT

By aeration, sponge superhydrophobicity can have a long sustainability in underwater environment.



ARTICLE INFO

Article history:

Received 5 November 2014

Received in revised form

21 December 2014

Accepted 22 December 2014

Available online 3 January 2015

Keywords:

Superhydrophobicity

Sponge

Sustainability

Aeration

Humidity

ABSTRACT

The air dissolution, together with vapor condensation, leads to short sustainability of superhydrophobicity, which turns out as a critical problem for the practical application in underwater environment. In this study, using sponge based superhydrophobic material as the prototype, we have tried to realize the long sustainable superhydrophobicity via an aeration strategy. To verify this protocol, firstly, the superhydrophobic sponge was obtained by grafting the hydrophobic moiety onto the backbone surface. Secondly, by connecting the partially immersed superhydrophobic sponge with the external atmosphere, the infinite air supply is achieved. Using air to flow in and out of the superhydrophobic matrix, vapor from the neighbor bulk water phase is carried out, so that water condensation is avoided. This leads to a long sustainability of the superhydrophobicity.

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1. Introduction

Superhydrophobicity, a phenomenon originated from the surface chemistry and topology, was primarily triggered by botanical studies [1]. Since it can escape from contamination from water and dust as the sacred lotus, it is also called lotus effect and under intense investigation for more than one decade [2]. Nowadays, having endured the primary material discovery and development stage, the practical application has been the leading orientation of this field [3]. All the usage of this extreme wettability is firmly

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correlated with water, which exists as droplet or bulk state. For the utilization targeting on water droplet, such as self-cleaning and antifogging, superhydrophobicity seems as a promising way. The underwater bulk state is also a wide realm for superhydrophobicity to involve in. With the research being put forward, attempts have been made to propel superhydrophobicity to use in this environment, since it can highly impact the processes occurring at the solid–liquid interface, e.g., gas exchange, fluid transport, drag reduction, anticorrosion and biofouling inhibition [4].

However, before the potentiality meets the reality, superhydrophobicity is facing a dilemma, i.e., short sustainability, in underwater environment. Ordinarily, if a surface has large contact angle ($>150^\circ$) and low hysteresis with droplet, it is regarded to perform excellent superhydrophobicity. Nevertheless, when immersed into water phase, the extraordinary wettability cannot remain long time and water will wet the surface. This exactly illustrates the performance difference between the droplet and the bulk water. In fact, static and additional pressure from water will induce the dissolution of the air entrapped, so that superhydrophobicity is experiencing a metastable state when contacting with water [5]. For water droplet lying on gas–solid–liquid interface, external atmosphere acts as infinite stock to replenish the dissolution occurring at air/water interface. However, for the routine film superhydrophobicity immersed in the bulk water, the reserved air amount is limited, and there is no supplement to offset the dissolution. When air continuously dissolves, superhydrophobicity will typically fail. Moreover, water condensation, encountered by both droplet and the bulk states, is another reason leading to the failure of superhydrophobicity [6]. The water vapor has the tendency to condense onto the solid surface, resulting in the decrement of the surface hydrophobicity. In turn, the external water will be facile to enter the matrix, and this will also accelerate the failure of the superhydrophobicity.

To achieve superhydrophobicity having long sustainability in underwater environment, the problems related to air dissolution and water condensation should be solved [7]. By analogizing the water droplet on a superhydrophobic surface, connecting the superhydrophobic surface with the external atmosphere is a simple route to realize the infinite air supply. For avoiding water condensation, the dynamic air flow can be employed to carry out the moisture from the superhydrophobic matrix, so that the vapor pressure will be smaller than supersaturation state in order to avoid the water condensation [8]. With this principle, the superhydrophobicity sustainability will be firmly elongated. However, the strategy cannot be applied to the routine film based superhydrophobicity, which is the major style material developed for years to exhibit this extreme wettability, since there is no pathway existing for air to go through and carry out the moisture. Luckily, the sponge based superhydrophobicity affords us an opportunity to try this protocol, since it exists as a self-standing bulk material with interconnecting free space to realize the easy entry and exit of air. In previous reports, superhydrophobic sponge is mainly introduced as an effective oil absorbent, due to the requirement of the occasional oil emission events [9], and its other potential applications have been largely neglected. In this study, using sponge based superhydrophobic material as the prototype, we have tried to realize the long sustainable superhydrophobicity via an aeration strategy. To verify this protocol, firstly, the superhydrophobic sponge was obtained by grafting the hydrophobic moiety onto the backbone surface. The superhydrophobicity is confirmed from theoretical and experimental backgrounds. Secondly, by connecting the partially immersed superhydrophobic sponge with the external atmosphere, the infinite air supply is achieved. Using air to flow in and out of the superhydrophobic matrix, vapor from the neighbor bulk water phase is carried out, so that water condensation is avoided. With the assistance of the in situ humidity

sensor, it is assumed that a long sustainable superhydrophobicity is achieved.

2. Experimental

The commercially available melamine formaldehyde sponge was cleaned in acetone and ethanol (A. G., Tieta Chemicals, Laiyang) successively to remove possible impurities. Then the sponge was etched in a mixed solution containing 147 g/L potassium dichromate (A. G., Ruijinte Chemical, Ltd., Tianjin) and 100 g/L H_2SO_4 (Tieta Chemicals, Laiyang) for 1 min. After cleaning with distilled water for several times, the sponge was dried in an oven for 2 h to make sure the complete evaporation of water. Then the as-dried sponge was immersed in a hexane (Tianjin Fuyu Fine Chemical Co. Ltd.) solution containing 10% (v/v) trichlorododecylsilane (Aldrich) for 2 h. After that, the sponge was brought out and squeezed the organic solution out. It was laid at room temperature for ca. 5 min until the hexane volatilized. To get rid of the remaining organic solvent, the as-obtained sponge was further dried at $60^\circ C$ for 2 h.

Before the characterization, the pristine and as-modified sponge was cut into pieces from bulk state to make sure the studied surface is randomly selected. Three-dimensional optical microscopy (Hirox 8700) and scanning electron microscope (SEM, Zeiss, ultra 55) were used to reveal the surface morphology of the sponge. The elemental composition was further achieved by energy dispersive spectroscopy (EDS, Oxford Instruments, X-max). The sponge wettability was measured by a contact angle meter (CAM-101, KSV Instruments) at room temperature ($25^\circ C$). Droplets of distilled water ($3\ \mu L$) were dropped at different places of the sponge surface and at least 10 readings were taken to determine average values. To evaluate the homogeneity of bulk state superhydrophobic material, the sponge was sliced with the blade into pieces for the contact angle measurement. For characterizing the affinity of water droplet to a tilt surface of the primary and as-modified sponge, contacting scenario was recorded by a digital camera (Cannon EOS600D).

For the sponge, it can be regarded as the compositing material of polymer and air. The free air volume in the sponge was measured using a water replacement method. By immersing the primary sponge ($10\ cm \times 7\ cm \times 3\ cm$) in water, the space previously occupied by air was taken by water. Before and after the soaking, the sponge weight was achieved using an electronic balance. The free air volume V in the sponge is calculated according to the following equation:

$$V = \frac{W_s - W_p}{\rho}$$

in which W_s , W_p and ρ represent as-soaked sponge weight, primary sponge weight, and water density, respectively.

To illustrate the aeration effect to the superhydrophobicity longevity, the as-modified sponge was partially immersed into water, and a pump (Minjiang Aquarium) was used for importing air to the sponge matrix. The aeration rate was set at 100 and 200 L/h, respectively. The room temperature and humidity was fixed at ca. $25^\circ C$ and 40%. The humidity sensor HDS10 as well as its calibration data was supplied by Lexiang Electronics, Guangzhou, China. An ACM Gill workstation was used for exerting the potential (0.8 V) and collecting the current.

3. Results and discussion

3.1. Morphology and elemental characterization of the pristine and as-modified sponge

The structure and elemental composition of the sponge is shown in Fig. 1. The optical microscopy reveals the macro- and micro-scale morphology. It is seen that the solid skeleton interconnects

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