



Preparation of thermally and chemically robust superhydrophobic coating from liquid phase deposition and low voltage reversible electrowetting



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ABSTRACT

Superhydrophobic surfaces and electrowetting have found applications in many fields. Two of the most desired features in these applications are a robust surface and low voltage actuation electrowetting. A thermally and chemically robust nano-scale superhydrophobic surface was prepared using facile techniques of sol-gel and hot water treatment to obtain rough pseudoboehmite alumina structures; and layer-by-layer coating, using Nafion®, to achieve the hydrophobization. It exhibited a contact angle of $167.2 \pm 0.8^\circ$; thermal stability of up to 300°C ; stability to acid, base, organic solvents and UV irradiation. Subsequently replacing Nafion® with 1H, 1H, 2H, 2H-perfluorodecyltrimethoxysilane and a conductive Au under layer coating, an extremely low voltage, 3 V, electrowetting and reversible electrowetting were achieved in air and dodecane media, respectively.

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1. Introduction

1.1. General introduction

Wetting is the ability of a liquid to maintain contact with a solid surface, when brought together. The phenomena of surface wetting and surface wetting tuning are of high interest in both academic and commercial application fields [1,2]. Applications of superhydrophobic surfaces (SHSs) include self-cleaning surfaces [3] and separation of liquid mixtures [4]. In the area of surface wetting tuning or electrowetting on dielectric (EWOD), they have applications in: digital microfluidics; liquid lens; micro-electricity generators and pixel units for electronic display units like TV sets, computers and e-paper; with typical actuation voltages in the range of 50–200 V [1,2,5–9].

1.2. Quantitative wetting

Wetting is quantified by contact angle (CA), θ , given by the Young equation, Eq. (1), derived by the balance of interfacial energies around

a liquid droplet on an ideal smooth surface:

$$\gamma_{LA} \cos \theta = \gamma_{SA} - \gamma_{SL} \quad (1)$$

where, γ_{LA} , γ_{SA} and γ_{SL} are the liquid-air (or surrounding environment), solid-air and solid-liquid interfacial free energies per unit area, respectively.

Conventionally, the wetting states of surfaces are classified into: *superhydrophilic*, *hydrophilic*, *hydrophobic* and *superhydrophobic*, when θ is $< 10^\circ$; $10^\circ < \theta < 90^\circ$; $90^\circ < \theta < 150^\circ$; and $\theta > 150^\circ$, respectively [11]. A non-wetting solid surface (i.e., $\theta \geq 90^\circ$) is normally obtained by coating it with a low surface free energy material, however, the maximum CA attained by this approach on a smooth surface is 119° [11]. Thus, obtaining a SHS involves a different approach of a combination of an appropriate surface roughness and low surface energy topography. For such surfaces, two models have been proposed for the quantification of the CA:

(1) the Wenzel model with CA, θ_w , given by,

$$\cos \theta_w = r(\gamma_{SA} - \gamma_{SL}) / \gamma_{LA} = r \cos \theta \quad (2)$$

where $r =$ (actual area of the rough surface) / (the projected area of the surface); thus $r > 1$.

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This model proposes that the droplet fills the spaces of the rough structures and forms a homogeneous wetting of the surface [12]; and

(2) the Cassie-Baxter model, with CA, θ_c , given by Eq. (3),

$$\cos\theta_c = f\cos\theta + (1-f)\cos\theta_f = f(\cos\theta + 1) - 1 \quad (3)$$

where f is the fraction of the solid surface area in contact with the droplet, i.e. $f < 1$.

The component $(1-f)$ is the fraction of fluid medium within the rough structures on which the droplet sits; and θ_f is the CA between the droplet and the fluid medium (for a fluid medium of air, $\theta_f = 180^\circ$, which gives the third component of Eq. (3)). This model has been proposed, with the assumption that the droplet sits on top of a composite of rough structures and fluid medium to form a meta-stable wetting state [13].

1.3. Electrowetting

Electrowetting (EW) [14] or EWOD [2,15,16], refers to the application of electric voltage to change the wettability of a polar or conductive droplet on a surface.

There are three major approaches to describing the EW phenomenon: classical thermodynamics, energy minimization, and electromechanical [1]. Jean Berthier [17], explaining from the electromechanical view point, writes that, in the presence of a DC or AC electric field, electric charges gather at the interfaces between the conductive and dielectric components of the set-up. The same electric field that induces these charges then couples with the interfacial charges to exert an interfacial force, and if the interface is deformable (such as the interface of a liquid and its gaseous surrounding), this force can distort the interface, thus, causing EW. These induced interfacial electric forces are especially strong on the liquid-gas interface at the vicinity of the triple contact line points (where the three adjacent phases (the droplet, the surrounding medium and the substrate) meet), due to the sharp wedges present at these points.

By the energy minimization approach, a built up electrostatic capacitive field destabilizes the Young's equilibrium forces acting on a droplet and the liquid droplet adjusts itself to restore a new balance. Based on this understanding, Berge [15] added an electrostatic capacitive energy component to the Young equation to obtain the basic EW equation, the Lippmann-Young equation, Eq. (4), for EWOD:

$$\cos\theta_v = \cos\theta + \varepsilon_0\varepsilon_r V^2 / 2d\gamma_{LA} \quad (4)$$

where, θ_v is the CA after voltage application; θ is the Young's CA; ε_0 is the permittivity of free space; ε_r is the dielectric constant of the insulating material; V is the applied voltage; d is the thickness of the dielectric component.

Eq. (4) is found to hold true until a threshold voltage, called CA saturation, beyond which CA does not change, but leads to dielectric material break down [5]. This observation has been reported in many research results [18–23].

Eq. (4) is for smooth surfaces. Torkelli [24] modified it for SHSs to obtain Eq. (5):

$$\cos\theta_v = \cos\theta_c + \varepsilon_0\varepsilon_r f V^2 / 2d\gamma_{LA} \quad (5)$$

where, f is the fraction of solid surface in contact with the liquid droplet.

Eqs. (4) and (5) suggest that when the voltage supply is turned off the wetted droplet should reverse back to its original state. However many research results show that EW in an air medium is usually irreversible. This has been explained to be due to both physical and chemical surface heterogeneity. Krupenkin et al. [25] explained that, during the electrowetting process, a sizable energy is dissipated for the system

to attain a new minimum energy equilibrium state and part of this energy is consumed to pin the droplet to the surface supporting it. Thus, preventing spontaneous reversibility when the voltage supply is removed. Halim et al. [26] reported that a solid-gas-liquid composite interface is replaced with a solid-liquid interface, i.e. indirectly inferring to dissipation of energy to form the new solid-liquid interface state.

Based on the above understanding, there are three proposed approaches to attaining reversible electrowetting (REW): 1) engineering roughening nanostructures, such as to minimize the energy dissipation in order to eliminate the energy barrier for transitioning back to the original state [26]; 2) providing energy to the system to replace the dissipated energy [25]; and 3) competitive two liquid wetting approach; where one liquid provides a lubricating effect to prevent the other from being pinned to the solid surface during EW. In our work we have used the competitive two liquid wetting approach.

1.4. Research motivation and hypothesis

In the field of SHSs and EWD, two of the major desires are, obtaining robust surfaces, and low actuation voltage, respectively.

For chemical modification to achieve SHSs, low surface energy organic polymers are commonly used. Materials with C–F bonds are the most effective for lowering the surface free energy because the F atom has the highest electronegativity and forms a stable covalent bond with carbon. Hare et al. [27] reported that the surface free energy increases when fluorine is replaced by other elements such as H and C, in the order, $-\text{CF}_3 < -\text{CF}_2\text{H} < -\text{CF}_2- < -\text{CH}_3 < -\text{CH}_2-$. Therefore, fluorocarbon polymers make excellent hydrophobic films and coatings; however, the adhesion between the substrate and the fluorine-based hydrophobic coating is via van der Waals forces and, thus, relatively weak [28]. Hence, we anticipated that Nafion®, with $-\text{CF}$, $-\text{CF}_2$ and $-\text{CF}_3$ groups (for low surface energy) and a sulfonyl group ($-\text{SO}_3^-$), will form a good hydrophobizing coating with strong ionic bonds to the pseudoboehmite substrate's reactive hydroxyl groups, with some preliminary treatment, to give a robust SHS.

For low actuation voltage for EW, silicon dioxide and parylene C are the commonly used dielectric materials used [29,30]: with examples of 60–70 V actuation voltages for 60 nm Teflon low surface energy coating on 800 nm parylene C [31,32]; and 25 V for a 20 nm Teflon coating on 100 nm silicon dioxide [30]. Ultrathin coatings have been avoided because they are more susceptible to electrical breakdown and have poor reliability [33]. Recently M. F. Samad et al. [3] have demonstrated an actuation voltage of 14.8 V, using a dielectric layer of polyvinylidene difluoride (PVDF) (1 μm) and a very thin layer (50 nm) of Teflon as the hydrophobizing coating.

In this paper, we have used ~300 nm of Au-rough alumina pseudoboehmite-FAS (fluoroalkyl silane; 1H, 1H, 2H, 2H-perfluorodecyltrimethoxysilane), coating to obtain a very low actuation voltage of 3 V, without dielectric material breakdown. In addition, we have employed facile and low-cost techniques such as sol-gel coating, hot-water treatment (HWT) and layer-by-layer (LBL) coating, unlike commonly used complex and expensive techniques like chemical vapor deposition, lithography, electrospinning, and specialty coating equipment [34,35].

2. Experimental details

2.1. Al_2O_3 sol preparation

The alumina sol preparation was adopted from Tadanaga et al. [36] as follows: typically, 6.0 g of aluminium *s*-butoxide ($\text{Al}(\text{O-sec-Bu})_3$) [Wako, 324–22475] was mixed with 10.98 g of isopropyl alcohol (IPA) [Wako®, min. 99.5%] and stirred at room temperature for 10 min at 700 rpm. A 4.76 g of ethyl acetoacetate (EAcAc) [Wako®, min. 98.0%] in 5.49 g IPA was added, as a chelating agent, with continuous stirring for 1 h. Finally, 0.88 g of water [from AQUARIUS Equipment: RFD

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