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Controllable wettability and morphology of electrodeposited surfaces on zinc substrates

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ABSTRACT

Superhydrophobic surfaces combining hierarchical micro/nanostructures were fabricated on zinc substrates by etching in hydrochloric acid solution, electrodeposition of ZnO coatings and subsequent thermal annealing. The optimal coatings were electrodeposited at −1.25 V for 900 s on the etched zinc substrates and then annealed at 200 °C for 60 min, which could achieve a maximum water contact angle of 170 ± 2° and an ultra-low sliding angle of approximately 0°. By conducting SEM and water CA analysis, we found that the morphology and wettability of prepared samples were controllable by the fabrication process. Interestingly, even without any additional modification, the samples prepared under different electrodeposition conditions (including $Zn(CH_3COO)_2$ concentration from 5 mM to 40 mM and deposition time from 300 s to 1500 s) exhibited superhydrophobic character. The influences of the $Zn(CH_3COO)_2$ concentration, deposition time, annealing temperature and annealing time on the wetting behaviors were also discussed in detail. Such superhydrophobic surfaces possess long-term stability, and good corrosion resistance as well as self-cleaning ability. In addition, the anti-icing properties of the ZnO films were investigated. These surfaces could be rapidly and reversibly switched between superhydrophobicity and superhydrophilicity by alternating UV illumination and dark storage or thermal annealing. The intelligent switchable surfaces with controllable wettability and morphology offer possibilities for chemical, biological, electronic and microfluidic applications.

1. Introduction

Surface wettability is a property of great importance in determining the application of solid materials, which is closely governed by surface chemistry and topographical microstructure. The surfaces with reversibly switchable wettability between superhydrophobicity (with water contact angle (CA) larger than 150°) and superhydrophilicity (with water CA less than 5°) have aroused tremendous interest due to their various unique applications in self-cleaning [1–4], biomaterials [5,6], sensor devices [7], ink-jet printing [8], intelligent microfluidic [9], controllable drug delivery [10] and lab-on-chip systems [11], etc. So far, materials with tunable wettability have been realized on polymers [12], metal oxides [13,14] and inorganic semiconductor oxides [15]. Under UV irradiation, the hydrophobic surface turns into hydrophilic. In the dark, the surface turns back to hydrophobic [16]. Among these materials, ZnO is a promising candidate in building functional electronic devices depending on its distinctive physical and chemical properties. Their properties and performance would be varied according to the adjustment of the shape, size, orientation, and density of ZnO. Thus, development of controllable synthesis of ZnO materials in morphology is urgently necessary for exploring the extension of ZnO.

Up to know, various shapes of ZnO nano- or microstructures such as nanowires [15,17], nanorods [18], nanotubes [19] have been reported. ZnO-coated superhydrophobic surfaces have been successfully achieved via numerous methods, including electrochemical deposition [20–23], chemical vapor deposition [24,25], thermal evaporation [26], self-assembly growth [27], hydrothermal method [28–31] and template method [32], etc. For instance, Izaki et al. [20] first proposed a wurtzite structure ZnO which was electrodeposited on ITO from $Zn(NO_3)_2$ solution at different voltages. Gong et al. [30] grew well aligned ZnO nanowire arrays on Si substrates via hydrothermal method modified with chain fluorinated organic compounds, after which it showed a water CA as high as 165°. Liu et al. [24] reported superhydrophobicity to superhydrophilicity of hierarchical ZnO film switched by

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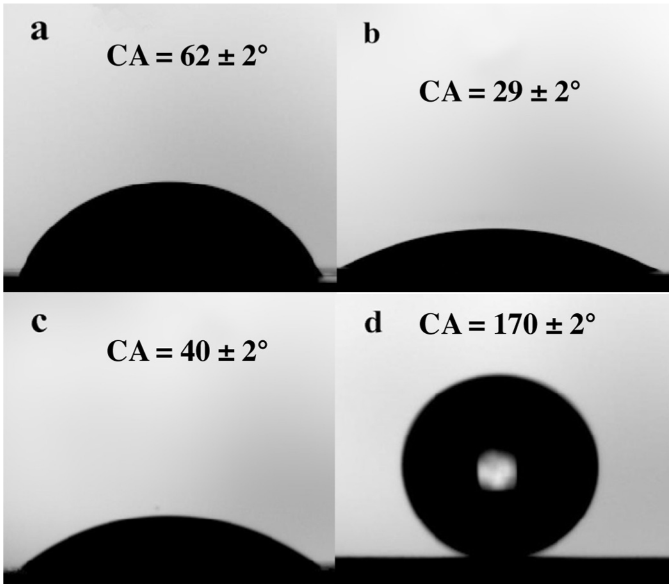

Fig. 1. Optical photographs of the water droplet on the zinc surface: (a) untreated zinc, (b) etched with 1 M HCl solution, (c) electrodeposited at −1.25 V for 900 s, and (d) after annealed at 200 °C for 60 min.

alternation of UV irradiation and dark storage, which was obtained directly via chemical vapor deposition method resulting in CA of 164°. Nevertheless, most of artificial methods require complicated operations and organic substances to achieve superhydrophobicity, and those modified surfaces may be damaged or contaminated easily during normal use. Therefore, electrodeposition is considered to be an effective technique for controllable fabrication of superhydrophobic ZnO surfaces due to its simplicity, low cost, low temperature growth and environmental friendly property.

Here, we propose a new method for fabricating ZnO-coated superhydrophobic surface on the zinc substrate. The ZnO coatings were obtained via electrodeposition followed by thermal annealing without any additional modification. The wettability, chemical composition, morphology, theoretical growth mechanism, stability, and corrosion resistance of the optimal superhydrophobic surfaces were investigated in detail. The influence of morphology and wettability with process conditions on prepared surfaces was systematically studied. Additionally, the anti-icing properties and reversible wetting transition between superhydrophobicity and superhydrophilicity of the samples were evaluated. This method is efficient for constructing surfaces with controllable wettability and morphology, which possibly show great potential in industrial application.

2. Experimental

2.1. Materials

Zinc acetate ($Zn(CH_3COO)_2$, 99.8%), potassium chloride (KCl, 99.5%), hydrochloric acid (HCl, 36–38%), acetone (C_3H_6O, 99.5%) and ethanol (C_2H_5OH, 99.5%) were purchased from Beijing Chemical Company. Zinc substrates were obtained from Beijing Cuibolin Non-Ferrous Technology Developing Co. Ltd.

2.2. Pretreatment of the zinc substrates

Zinc substrates (2.0 cm × 1.0 × cm × 0.1 cm, Beijing, 99.999%) were ultrasonically cleaned in ethanol, acetone and deionized water in sequence for 5 min to remove the greasy dirt. The cleaned surfaces were etched in 1 mol L^{-1} hydrochloric acid (HCl) solution for 4 min at room temperature to remove the zinc oxide layer and organic contaminants. After that, the samples were rinsed with deionized water rapidly to get rid of any residual acid, and dried in air.

2.3. Fabrication of the superhydrophobic surfaces

Electrodeposition was carried out in a classical three electrodes cell with platinum foil as counter electrode, saturated calomel electrode (SCE +0.242 V vs. SHE) as reference electrode, the pre-treated zinc sheet with an exposed area of 1 cm^2 as working electrode in the electrolyte. The pre-treated zinc sheet and platinum foil with the same size were positioned parallel with a distance of 10 mm. The electrolyte was an aqueous solution containing $Zn(CH_3COO)_2$ (10 mM) and KCl (0.3 M), in which KCl was added as the supporting electrolyte to increase the conductivity. Then, electrodeposition of the coatings were prepared at applied voltage potential of −1.25 V determined by cyclic voltammetry (CV) for 900 s (Figs. S1 and S2). After deposition, the samples were rinsed with deionized water and dried in air. Subsequently, the as-deposited samples were put into Petri dish, followed by annealing at 200 °C for 60 min in the oven, and then kept in unplasticized poly vinyl chloride (UPVC) tubes for further experiments.

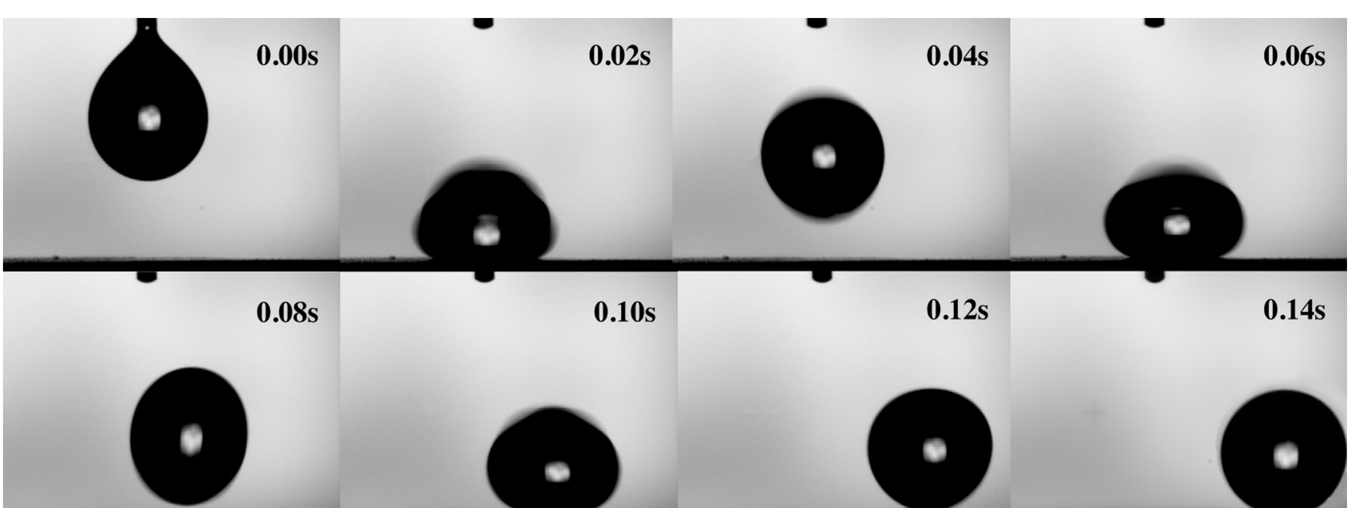

Fig. 2. Successive snapshots of a water droplet dropped onto the superhydrophobic surface.