Research Article



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Superhydrophobic organic-inorganic thin films on aluminum by a simple one-step electrochemical process

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Abstract

An ethanolic solution containing copper nitrate salt and stearic acid (SA) organic molecules have been used to perform electrochemical modification of aluminum surfaces using a DC voltage to render them superhydrophobic in a one-step process. The formation of low surface energy copper stearate thin film having rose petal like micro-nano morphology is the driving force on the roll-off properties of water drops on these surfaces providing superhydrophobic properties with water contact angle of $162 \pm 1^\circ$, and an excellent corrosion resistance property.

Introduction

Wettability is one of the most important surface prosperities of the solid materials, which is governed by both the chemical composition and geometric structure of a surface. In nature, the most widely known example is the lotus leaf owing its self-cleaning properties due to the coexistence of micro-nanostructure and low surface energy waxy coating that weakens the electrostatic interaction between water and surface [1]. Due to the versatile applications of superhydrophobic surfaces researchers all around the world is are continuously working in this field of research [2-6]. Our group is actively working in the fabrication of superhydrophobic surfaces on aluminum and other metal surfaces using different techniques [7-17]. For example, we have previously shown that copper surfaces can be made superhydrophobic by a simple one-step electrochemical process. This one-step procedure, is not only low cost, facile and effective, but the micro-nanostructured texture of the surface can also be easily controlled by regulating the parameters of electrodeposition such as the electrolytes concentration, deposition time and applied DC voltage [12,17]. However, this method failed to modify the aluminum surfaces superhydrophobic as aluminum is not reactive like copper and does not produce aluminum stearate by this method [16]. Therefore, initially we electrodeposited microdots of copper on aluminum surface and then modified the copper deposited aluminum surface using the electrochemical process which resulted in superhydrophobic properties, however, employing more than one step in the fabrication process [15].

In this letter, this complexity has been overcome and a solution has been provided to obtain superhydrophobic aluminum surfaces by a one-step electrochemical modification of aluminum substrates in an ethanolic stearic acid solution containing copper nitrate salt. Chemically cleaned aluminum plates were taken as both cathode and anode in an ethanolic stearic acid (SA) and copper nitrite mixed solution and a DC voltage of 10 V was applied to the electrodes separated by a distance of 1.5 cm. The molar ratio of Cu^{+2}/SA was kept to a constant value of 0.5 in this present work. The process resulted in the growth of a thin film on the cathodic electrode. The morphological chemical and wettability analysis on the electrochemically growth thin films on aluminum surfaces were performed using the morphological analyses of the samples were performed using a scanning electron microscope (SEM, JEOL JSM-6480 LV). Optical profilometry (model: was also used to measure the topography and surface roughness. The chemical composition was analyzed by X-ray diffraction (XRD, D8 discover with Cu Ka wavelength 0.154 nm) and Fourier Transform Infrared spectroscopy (FTIR, Agilent Cary 630). The wetting characterization of the sample surfaces was carried out by measuring static and dynamic contact angles using a First Ten Angstrom contact angle goniometer (the static contact angle has been abbreviated as CA and the dynamic contact angle has been abbreviated as contact angle hysteresis (CAH)). The corrosion studies were performed by electrochemical impedance spectroscopy (EIS) in the frequency range between 10 mHz and 100 kHz with a sine-wave amplitude of 10 mHz using 3.5 wt.% NaCl aqueous solution.

A optimization process

Figure 1a shows high angle x-ray diffraction (XRD) spectrum of the thin film on aluminum surface deposited for 10 min and Figure 1b, the inset of Figure 1a, shows the low angle XRD spectrum of the same. The high angle XRD shows four characteristic peaks of aluminum [18] and the low angle XRD spectrum prove that the thin film is the copper stearate as we reported earlier on copper surfaces [12,19] The characteristic copper stearate peaks are identified by triangular legends in Figure1b. Figure 1c shows the FTIR spectra of chemically cleaned Al substrate and that of the thin films on aluminum surfaces prepared with varying times of 1, 10 and 60 minutes. Due to the metallic nature of the chemically cleaned Al surface, no characteristic peaks of FTIR are

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Figure 1. (a, b) XRD spectra, both high and low angle, of thin films on aluminum surface (c) The FTIR spectra (1) chemically cleaned Al substrate, and superhydrophobic aluminum surface prepared for (2) 1 min, (3) 10 min and (4) 60 min;

visible (Figure 2c-1) on this surface indicating the removal of the native oxide of aluminum. This is also due to the fact of the detection limit of FTIR to probe the native surface oxide. On the other hand, Figures 1c-2,3 and 4 of the thin films on aluminum surfaces show intense bands centered at 2954 cm⁻¹, 2918 cm⁻¹ and 2848 cm⁻¹ these are assigned to be the asymmetric stretching of -CH, as well as symmetric and asymmetric stretching vibrations of -CH₂ from stearic acid [17]. The peaks at the 1589 cm⁻¹ and 1467 cm⁻¹ are attributed to the -COO band due to the formation of thin films of copper stearate on the aluminum surface [17]. These spectra also show that the intensity of these peaks increases with the increase in the time of electrochemical modification. The presence of these peaks confirms the formation of the low surface energy copper stearate which is agreement with our previous report on copper surfaces [17]. Based on these analyses, a probable formation mechanism thin film of copper stearate on the aluminum surface can be derived as follows:

$$Cu^{+2} + 4 COOH - (SA1) = 2 Cu (COO - SA1)_2 + 4H_2$$

where, the compound Cu(COO-SA1) is called copper stearate, where SA1= -(CH₂)₁₆-CH3.

The Scanning Electron Microscopy (SEM) image of the chemically cleaned aluminum surface presented in Figure 2a shows that the surface is composed of round micro-nano craters of varied sizes. The inset of Figure 2a shows the image of water drop with a contact angle (CA) of 54°. SEM image in Figure 2b shows the morphological feature of the copper stearate thin films on aluminum surface grown for 1 minute in the form of microflowers of diameter less than 5 µm assembled with many nanoscaled features. The inset of Figure 2b shows the image of water drop with a contact angle (CA) of 144°. It can be seen from the Figure 2c that the aluminum substrate is completely covered by the copper stearate thin films presenting a rose-petal-like microstructured morphology when the electrochemical modification time is increased to 10 min. The standing micronano-petals construct the porous structure that entraps the air beneath a water drop hence enhancing the roll off properties of the superhydrophobic surfaces providing water contact angle of $162 \pm 1^{\circ}$ (in the inset of Figure 2c and a water contact angle hysteresis (CAH) below 1.7 \pm 1°. The prolongation of electrochemical modification time to 60 min leads to a compact thin film Figure 2d with the absence of the rose-petal-like

microstructures leaving no room for entrapment of air to boost the water drop roll-off property. Consequently, the water contact angle reduced to ~145(in the inset of Figure 2d with CAH above 10° on this compact surface. As evident from the time dependent morphological evolution, the surface roughness of these surfaces also increase with the increase of electrodeposition time from 0 to 10 min and then decrease with further prolongation of modification time to 60 min complementing the morphological behavior. The roughness, measured by optical profilometry, reached to the highest value of \sim 3.61 µm when the deposition time was 10 min. Figure 2e shows the variation of the water contact angle (CA) with the electrochemical modification time indicating the optimum deposition time to be 10 minutes to obtain the best superhydrophobic properties. Figure 2f shows the Nyquist plots, one of the presentations of EIS studies, a graphical presentation of real part of the impedance, Z', vs imaginary part of the impedance, Z". The charge transfer resistance (Rct) as derived from these plots are found to be 1130 k Ω cm² and 1.56 k Ω cm² for the superhydrophobic thin films on aluminum grown for 10 min and aluminum substrate, respectively. It can be noted that the value of the Rct for superhydrophobic surface is 700 times larger than that of the chemically cleaned Al. In a recent work by Liu et al. [20], the Rct of the superhydrophobic cerium containing myristic acid on copper alloys (brass) was reported to be 10 times larger than their as-received brass substrate. It is to be noted that the Nyquist plots of both superhydrophobic thin films on aluminum and aluminum substrate have a linear part at low frequencies (last few data in the graphs) due to the capacitive nature of these surfaces in corrosion environment associated to Warburg impedance. A complete study on the effect of composition as well as potential on the superhydrophobic and corrosion properties is currently in-progress to be communicated as a regular article.

A facile one-step electrochemical modification process has been developed to prepare superhydrophobic aluminum surfaces via electrochemical modification using an ethanolic solution containing copper nitrite and stearic acid. The surface morphology, roughness and wetting properties are found to vary with the electrochemical modification time. The optimum surface presenting the best superhydrophobic properties consists of rose petal-like microstructures of copper stearate, as evident from FTIR and XRD analysis, contributing to a very high water contact angle of $162 \pm 1^{\circ}$



Figure 2. SEM images of (a) chemically cleaned aluminum substrate; and electrochemically modified aluminum substrates at 10 V for (b) 1 min, (c) 10 min and (d) 60 min, keeping the molar ratio of Cu⁻²/SA equal to 0.5; (e) variation of water contact angle (CA) with electrodeposition time, (f) Electrochemical impedance spectroscopy (EIS), Nyquist plots, of chemically cleaned aluminum, as (a) and superhydrophobic surface as (c).

with excellent water drop roll-off properties. The electrochemical impedance spectroscopy (EIS) analysis shows that the charge transfer resistance of the superhydrophobic surface is 1360 k Ω -cm² which is 700 times larger than the chemically cleaned aluminum surface.

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