Fabrication of Superhydrophobic Nanostructured Surface on Aluminum Alloy

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Abstract

A superhydrophobic surface was prepared by consecutive immersion in boiling water and sputtering of polytetrafluoroethylene (PTFE or Teflon®) on the surface of an aluminum alloy substrate. Immersion in boiling water was used to create a micro-nanostructure on the alloy substrate. Then, the rough surface was coated with RF-sputtered Teflon film. The immersion time in boiling water plays an important role on surface morphology and water repellency of the deposited Teflon coating. Scanning electron microscopy images showed a "flower-like" structure in first few minutes of immersion. And as the immersion time lengthened, a "corn-flake" structure appeared. FTIR analyses of Teflon-like coating deposited on water treated aluminum alloy surfaces showed fluorinated groups, which effectively reduce surface energy. The Teflon-like coating deposited on a rough surface achieved with five-minute immersion in boiling water, provided a high static contact angle (~164 º) and low contact angle hysteresis (~4 º).

Keywords

Superhydrophobicity, boiling water, RF-sputtering, Teflon, aluminum alloy

Introduction

Recently, superhydrophobic surfaces (water contact angle $\theta > 150^{\circ}$) with a low contact angle hysteresis have attracted much attention for industrial and biological applications such as antibiofouling surfaces, reduction of ice and snow adhesion, self-cleaning surfaces, stain resistant textiles, antisoiling architectural coatings, corrosion prevention and reduced surface friction for microfluidic channels [1-2]. It has been shown that the maximum contact angle that can be attained on a flat surface by lowering the surface energy does not exceed 120° [3]. However, the addition of roughness to the surface can increase the contact angle of water without altering surface chemistry. So, superhydrophobic surfaces can be achieved by a combination of low surface energy materials, and surface micro- and nanostructures. Various approaches have been developed to create superhydrophobic surfaces, such as the sol-gel process, plasma treatment, electrochemical method, template method, vapor deposition, layer-by-layer method, and others [4-10].

These methods generally necessitate extensive materials, facility costs and/or raise environmental concern. Therefore, developing a simple, inexpensive approach to obtain an industrially feasible superhydrophobic surface is important and necessary. In this work, an aluminum alloy surface was treated with boiling water for developing nanopore structure films. This method is called boehmitage (formation of boehmite, $Al_2O_3.H_2O(s)$), and is used industrially to improve the corrosion properties of aluminum. Low surface energy coatings can be produced by deposition of low surface-energy materials such as fluorocarbons and silicones precursors [11-13]. Polytetrafluoroethylene (PTFE or Teflon®) is actually one of the best candidates due to its low electrical permittivity of ~ 2.1, low surface energy and chemical stability [14]. However, PTFE is very difficult to deposit as a thin film principally because it does not dissolve readily in any solvent, which prevents spin-coating deposition. On the other hand, a variety of CVD and PVD techniques have been used to deposit PTFE. The sputtering technique is widely used in electrical and mechanical applications because the process is simple, time saving, environmentally friendly, and the resulting coating has a uniform structure and excellent adhesion properties to most substrates [15-16]. In this work, a superhydrophobic surface with low contact angle hysteresis (CAH) was made by consecutive immersion in boiling water and sputtering of Teflon on the surface of aluminum alloys.

Experimental section

Mirror-polished 6061 aluminum alloy coupons were used as the substrate. The samples were boiled in distillated water to roughen the surfaces. To achieve different roughness levels, the duration of boiling was varied. The RF plasma-sputtering process was carried out in an HICP-600SB PECVD system, manufactured by Plasmionique Inc. The aluminum alloy surface was pre-cleaned and pre-activated in 50 W with argon flow rate of 50 sccm for 5 minutes at 1.3 Pa. After cleaning by plasma argon, the sputter deposition process was carried out at 50 W RF power for 20 minutes at 2.6 Pa.

Sample surface morphology was examined using a LEO field emission scanning electron microscope (FESEM) and an atomic force microscope (AFM) (Digital Nanoscope IIIa by digital instruments). Water contact angle measurements were carried out using a Kruss DSA 100 goniometer (double distillated water drop volume ~ 4 μL). Contact angle hysteresis was measured using a common experimental procedure [17].

FT-IR spectra were measured on a Fourier transformation infrared spectrometer (Perkin-Elmer, Spectrum one). The reflected beam was collected for 24 scans at a resolution of 4 cm^{-1}. Polished aluminum alloy was used as the reference.

Results and discussion

The FE-SEM images, displayed in Figs. 1a-1c, for aluminum alloys immersed for 3, 5 and 10 minutes show various structural features. Figure 1a exhibits a fine “flower-like” structure with 20-150 nm petal size. By increasing the boiling-water immersion time (Fig. 1b), the petal size became wider and cell-wall thickness increased. The 10-minute treatment shows the “corn-flake” structure with cell wall thickness of about 10 nm and 20 to 100 nm petal size (Fig. 1c) [18-19]. Figure 1d shows the aluminum alloy covered by a RF-sputtered PTFE thin film after a 5-minute immersion in boiling water. Comparing with Fig. 1b, the surface asperities have relatively flat and shallow tops and the depth of the nanopores is slightly decreased after the PTFE thin film deposition. However, the “flower-like” structure is still present after the PTFE deposition.

(Fig. 1)

Figures 2a-2d are AFM images of the polished aluminum alloy and aluminum alloy treated in boiling water for different times. A smooth surface with a roughness of around 2.2 nm was observed for the polished aluminum alloy surface. However, once boiled in water, the surfaces developed needle-like structures. The height of such structures varied with boiling time. Theses images show that the surface roughness is strongly depended on the immersion time and surface roughness varied from 28 to 52 nm for boiling times of 3 and 10 minutes, respectively. Kurtosis values (R_{ku}) of the boiled samples are around 3, which indicate Gaussian distribution and random surface. The roughening process can be attributed to chemical erosion of the freshly polished aluminum alloy surface by water at high temperature [6]. After deposition of a PTFE coating on the boiled samples, the surface became smoother and surface roughness of the PTFE deposited on the boiled samples for 3 and 10 minutes decreased to 23 and 45 nm, respectively.

(Fig. 2)

Figure 3 shows the FT-IR spectra of the aluminum alloy immersed in boiling water for different times and the Teflon-like coating deposited on the surface immersed in water for 5 minutes. There is a broad peak at 3420 cm^{-1} with an unresolved shoulder at 3120 cm^{-1}. These peaks are attributed to the hydroxyl stretching mode. The peak seen at 1070 cm^{-1} is attributed to hydroxyl bending vibration [20]. At 2-minute immersion time, only the weak peak at 3420 cm^{-1} was seen. As the immersion time increased, the 3420 cm^{-1} peak shifted to 3300 cm^{-1} and the shoulder moved into a peak at 3100 cm^{-1} [21]. Peaks appeared at 1630 cm^{-1}, due to bending mode of interstitial water, at 750 cm^{-1} and 620 cm^{-1}, due to Al-O stretching vibration. [22]. New peaks appeared on the FTIR spectra of Teflon deposited on the aluminum alloy treated in boiling water for 5 min (upper spectrum). Peaks related to asymmetric C–F stretching (1150 cm^{-1}), and CF_2 symmetric stretch vibrations (1242 cm^{-1}) and a weak peak of CF_3 vibrations (991 cm^{-1}) [4, 23] also appeared.

(Fig. 3)

Figure 4 shows the evolution of the static contact angle of Teflon-like coatings deposited on aluminum alloy surfaces as a function of immersion time. The contact angle of a Teflon-like coating deposited on a polished aluminum alloy surface (without water treatment) is about 114±1°. While the RF-sputtered PTFE coating on the aluminum alloy immersed in boiling water showed superhydrophobic behavior. The water contact angle was about 161±3° for a 30-second immersion time. By increasing the immersion time, the contact angle increased to 164±2°, and for immersions of more than 15 minutes, the contact angle decrease.

(Fig. 4)

Measurement of the hysteresis contact angle is very important to properly characterize the superhydrophobic surface [24]. For instance, a high contact angle water droplet deposited on a horizontal surface may remain pinned until the surface is tilted to a considerable angle [25]. Therefore, the static contact angle alone is not enough to reflect the real wettability of a solid surface [6]. Wenzel and Cassie-Baxter are the two main models that attempt describe the wetting of textured surfaces [26, 27]. In Wenzel's model (homogenous interface), the liquid droplet retains contact at all points with the solid surface below it. Concerning the Cassie-Baxter model (composite interface), air pockets are trapped in the rough surface cavities, resulting in a composite solid–liquid–air interface, as opposed to the homogeneous solid–liquid interface. The evolution of contact angle hysteresis of Teflon-like coatings with immersion time in boiling water is shown in Fig. 5. The contact angle hysteresis decreased by increasing the immersion time to 3-5 minutes. Immersion times above 5 minutes led to increased contact angle hysteresis.

In fact, study of the boiling-water-produced film demonstrated that the structure of this film depended on the treatment time. Alwitt explained that when aluminum was immersed in boiling water, the hydrated oxide film produced would be pseudoboehmite with the composition $Al_2O_3\ 2.1H_2O$ [20]. The film growth process in the temperature range of 50-100º C was defined in three stages, which included an incubation period (1-2 sec.), a period of rapid growth, followed by a slow growth stage after the first few minutes of immersion. At these temperatures, bayerite crystals first appear at still longer times and their growth would constitute the final stage. So, the decrease in static contact angle and the increase of contact angle hysteresis could be explained by the increase of roughness and variation of surface morphology in the second and third stages of film growth. Also, the needle-like structure observed for immersion times of 3-5 minutes may serve as a means of trapping sufficient air for low sliding angles to be exhibited.

(Fig. 5)

In fact, it is now usually accepted that coatings having CAH < 5^o are strongly icephobic [28]. In the light of these promising results, future works will focus on the icephobic properties of these coatings.

Conclusion

Superhydrophobic surfaces were derived using two simple industrial processes. Nanostructured patterns were created on aluminum alloy surfaces by immersion in boiling water. The rough surface was coated with RF-sputtered polytetrafluoroethylene.

The morphology of these surfaces showed that nanostructure and surface roughness are strongly dependent on immersion time. SEM images showed a “flower-like” structure following 3-5 minutes of immersion in boiling water. Increasing the immersion time, led to a “corn-flake” structure. AFM analysis of samples treated for 3 minutes and 10 minutes showed that the RMS roughness varied from 28 nm to 52 nm. FTIR analyses showed fluorinated groups, which contribute to the low surface energy of Teflon coatings. The Teflon coating deposited on rough and needle-like structures obtained from 5-minute immersion provided a high static contact angle (~164 º) and low contact angle hysteresis (~4 º) by means of entrapment of a greater amount of air.

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Figure captions:

Figure 1: SEM micrograph of the film produced on aluminum alloy immersed in boiling water for (a) 3 min (b) 5 min (c) 10 min (d) 5 min and covered by PFTE coating

Figure 2: AFM images of (a) polished aluminum alloy surface (R_q=2.2 nm), (b) aluminum alloy boiled in water for 3 min (R_q=28 nm, R_{ku}=3.6), (c) aluminum alloy boiled in water for 5 min (R_q=33 nm, R_{ku}=4.5), (d) and aluminum alloy boiled in water for 10 min (R_q=52 nm, R_{ku}=3.5)

Figure 3: FTIR spectra from aluminum alloy for immersion times of 2, 3, 5 and 10 min in boiling water. The upper spectrum corresponds to Teflon coating deposited on an aluminum alloy surface immersed in boiling water for 5 min.

Figure 4: Evolution of static water contact angle of RF-sputtered Teflon coating deposited on water-treated aluminum alloy surface versus immersion time in boiling water

Figure 5: Variation of contact angle hysteresis of Teflon-like coatings deposited on treaded aluminum alloy in boiling water vs. time of immersion in water

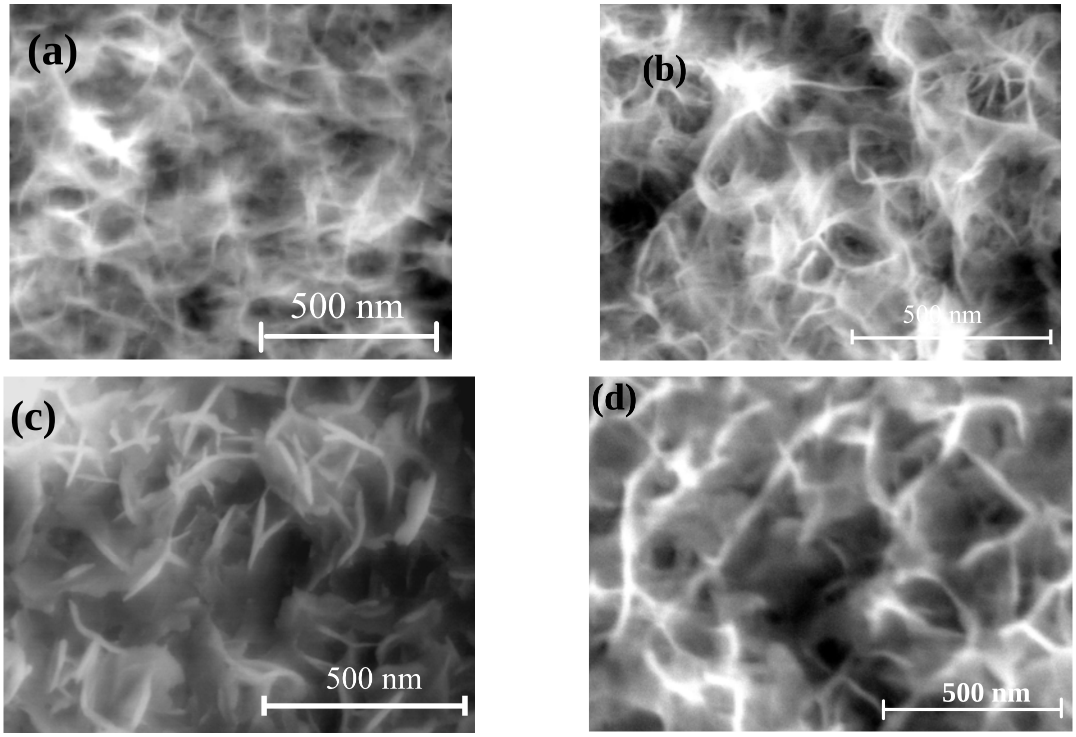
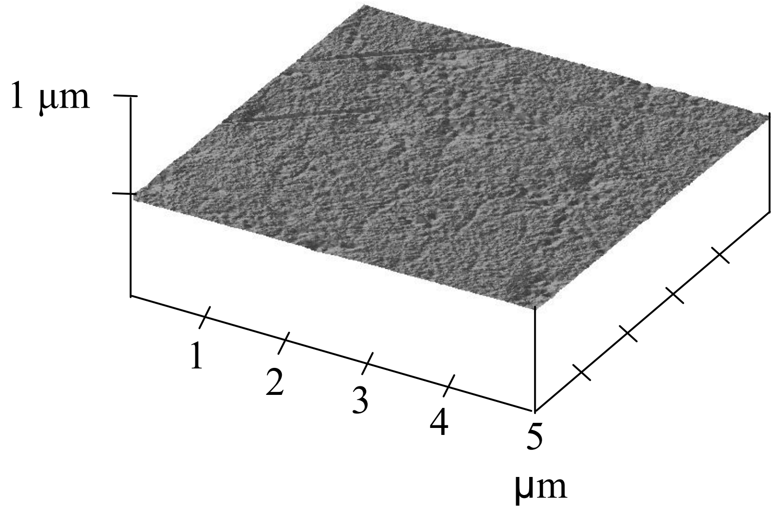
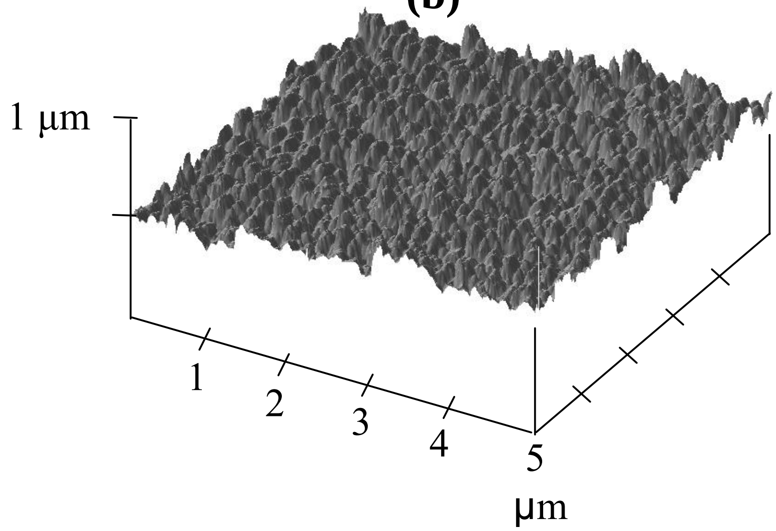


Fig. 1

(a)



(b)



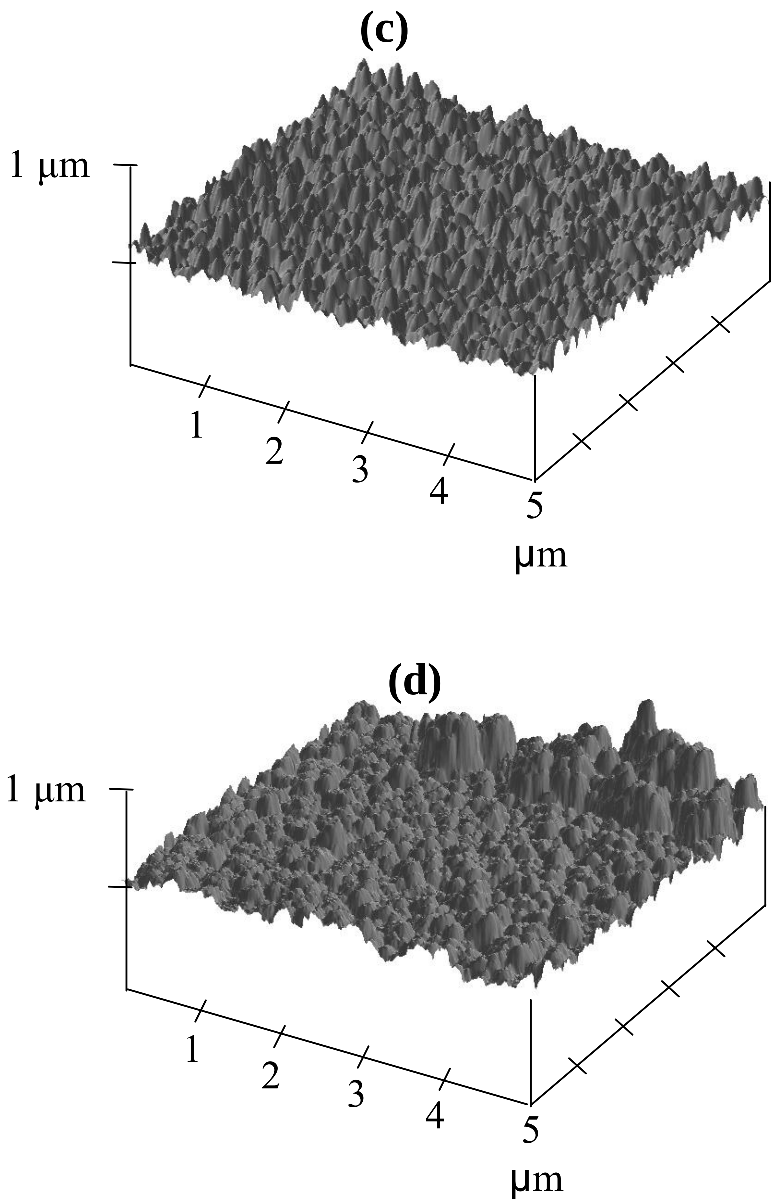


Fig. 2

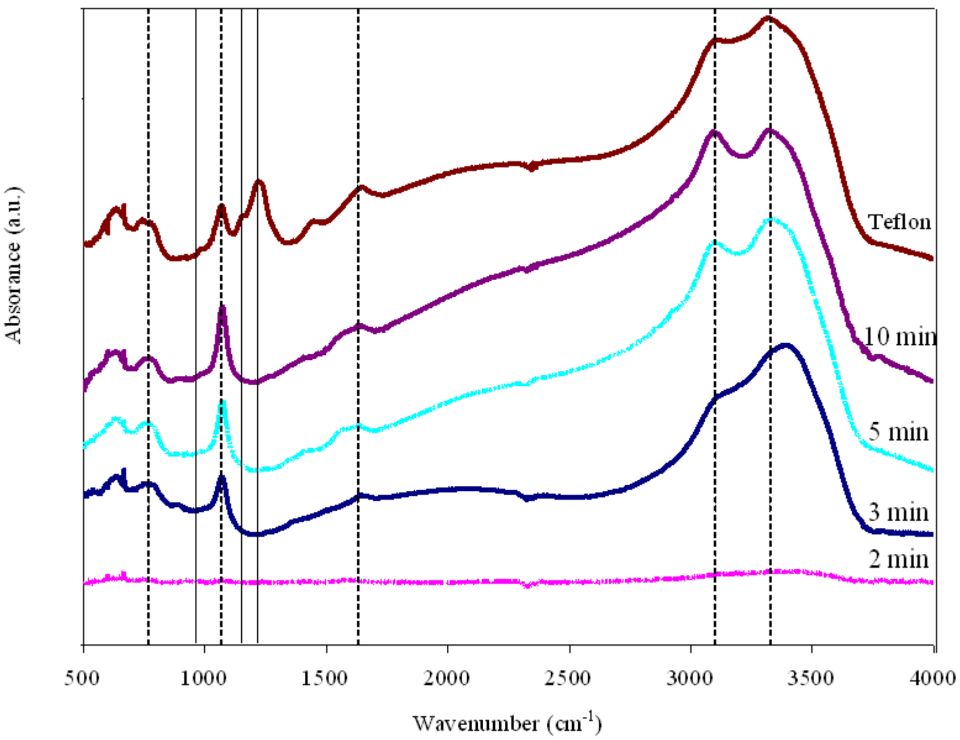

Absorance (a.u.)
Teflon
10 min
5 min
3 min
2 min
500
1000
1500
2000
2500
3000
3500
4000
Wavenumber (cm-1)

Fig. 3

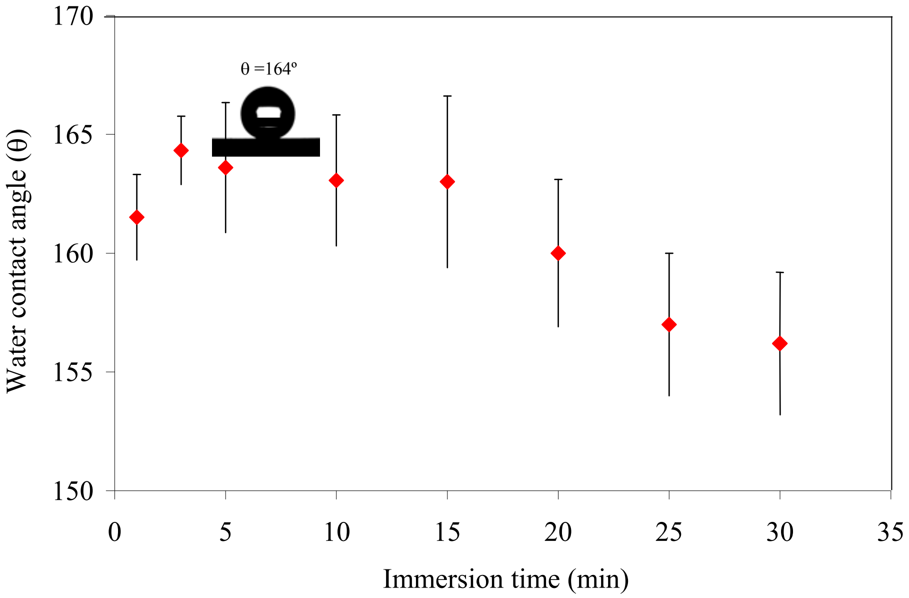

θ =164º
170
165
160
155
150
Water contact angle (θ)
0
5
10
15
20
25
30
35
Immersion time (min)

Fig. 4

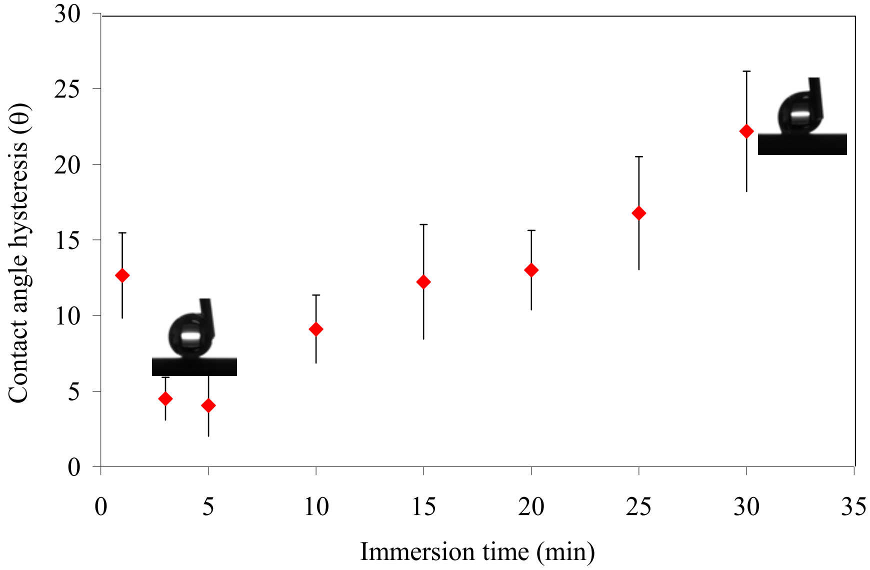

30
25
20
15
10
5
0
Contact angle hysteresis (θ)
0
5
10
15
20
25
30
35
Immersion time (min)

Fig. 5