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Silane decorated metallic nanorods for hydrophobic applications

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ABSTRACT

A novel technique to modify a metallic surface for anti-icing applications is presented. An oblique angle deposition (OAD) technique has been used to fabricate metallic nanorods of Aluminum and Tungsten on a glass substrate. A conformal coating of a silane has been applied using a molecular vapor deposition technique. The resulting surface has shown a static contact angle of 134° with the water droplet. SEM, AFM and XPS have been used to study the surface modification. This is a highly promising approach for anti-icing applications due to its scalability at a very low cost.

1. Introduction

Super hydrophobic surface finds many applications in different fields of science and technology. The aerospace industry is one such field that can take the advantage of superhydrophobicity for anti-icing coatings. Various approaches have been used to generate a super hydrophobic surface such as sol gel method [1,2], plasma polymerization [3], optical lithography [4], inkjet printing [5], mechanical polishing and chemical etching [6], controlled fluorination of nanoparticles [7], etc. However, it is a great challenge to obtain super hydrophobic state on the entire body of the airplane as the coating must be strong enough to sustain abrasion from impacting water droplets in rain in flight, and must operate effectively with other chemicals common in the aerospace environment. Hence, the coating for such applications requires their mechanical properties have high adhesion to the surface of the body and can sustain the high impact and erosion stress. Aluminum and its alloys have been extensively used in aerospace structural applications for their excellent mechanical properties and lightweight. However, normal smooth Al surface is hydrophilic with a water drop contact angle in the range of 50–55° depending on the smoothness of the surface. Several efforts have been carried out to modify Al surfaces to exhibit hydrophobicity [8–11]. However, such methods have proved inadequate in terms of scaling up to a large area and sustainability under severe conditions. For example, Sarkar et al. [12] have showed an ultrathin coating of Teflon on a chemically etched rough surface of Al can exhibit a contact angle of 164° with water. Although, such a method has a potential for scaling up, the ultrathin Teflon could easily wear out under the rugged conditions of airplane operation and can form an active spot for ice-buildup. In this paper, we present a novel technique to modify a metal surface for anti-icing applications without changing its other physical properties. The idea of generating a rough surface through metallic nanorods and subsequent silane decoration is schematically shown in Fig. 1. We have chosen Al and W as test materials for their potential in aerospace applications. Oblique angle deposition (OAD) technique has been used to fabricate Al and W nanorods. The surface energy of the nanorods was reduced by decorating a monolayer of a silane. The resulting contact angle has shown a promise for anti-icing application.

2. Experimental

Aluminum and tungsten metallic nanorods were grown on a glass substrate using the OAD technique. Several researchers have used OAD sputtering to fabricate nanorods of different materials [13–15]. A glass substrate was mounted on a rotating sample holder. The sample holder was tilted in such a way that the substrate normal makes an angle of 85° with the target normal.

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14. ABSTRACT
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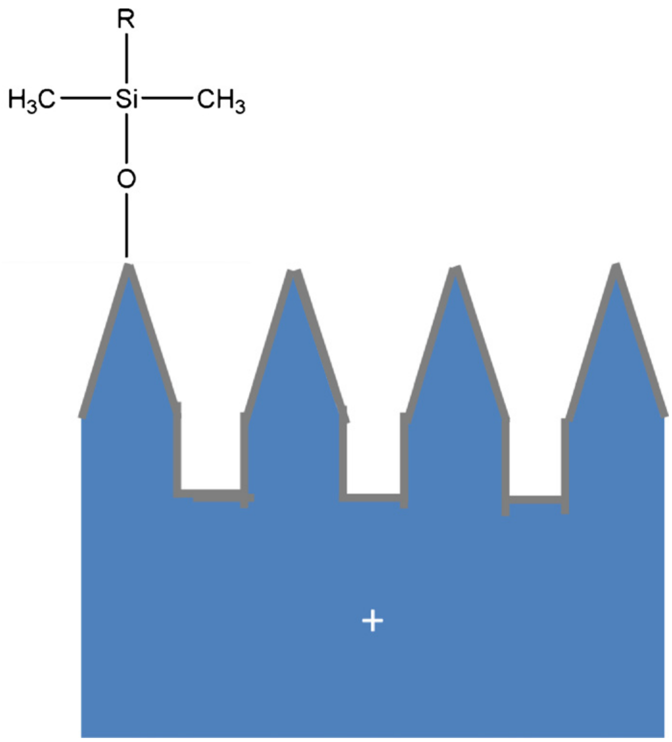

Fig. 1. A schematic of metallic nanorods decorated with FOTS (thin layer in black color is FOTS).

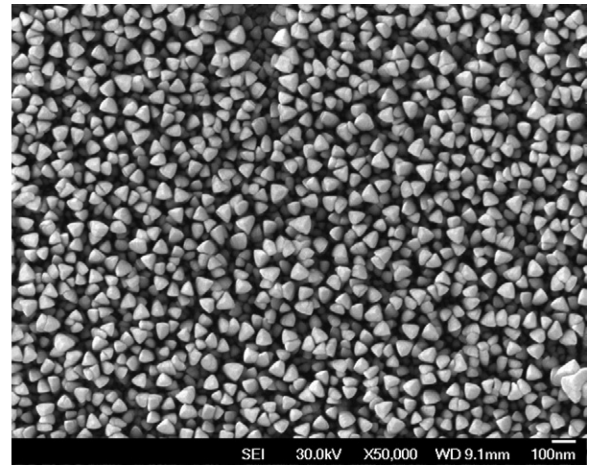

Fig. 2. SEM image of W nanorods grown on a glass substrate.

The sample was rotated at a speed of 3 rpm during the deposition. For both W and Al deposition, the chamber was pumped down to a base pressure of 5×10^{-7} Torr using a turbo molecular pump. Ar gas was used to generate plasma at 2.5 mTorr pressure. The sample–substrate distance was 15 cm. The power density for W was 5 and 3.5 Watt/cm^2 for Al. The observed deposition rates for W and Al were 5 and 7 nm/min, respectively. Tridecafluoro-1,1,2,2-Tetrahydrooctyl-Trichlorosilane, commonly known as FOTS (Gelest Inc.), was deposited at 0.7 Torr pressure on W and Al metallic nanorods using molecular vapor deposition technique (MVD-100, Applied Microstructures in Cornell Nanoscale Facility, Ithaca, NY). A longer reaction time of 30 min was given to make sure that monolayer modification had been occurred uniformly all over the sample. The micro structural properties were studied using JEOL700 Scanning Electron Microscope and Nanoscope 3100 Atomic Force Microscopy. The static contact angle of a water droplet was measured at 25 °C using a VCA Contact Angle Goniometer. The XPS data were obtained on a Thermo Scientific K-Alpha X-ray photoelectron Spectrometer at a background pressure of 5×10^{-9} Torr, using a Al Kα ($h\nu$ = 1486.6 eV) X-ray source. The x-ray beam used was 400 μm in diameter. The collected data were referenced to the C 1s peak to 285 ± 0.5 eV. Wide survey scans were collected from 0 to 1350 eV at a pass energy of 200 eV in 1 eV steps with a 50 ms dwell time to determine overall elemental composition. The relative atomic concentrations of the detected elements were calculated and normalized to 100% using sensitivity factors supplied by the instrument manufacturer from known certified standards. Detection limits for XPS are approximately 0.1–1.0 at% depending upon the sensitivity of the elements. The escape depth of the ejected photoelectrons is in the order of 50–100 Å, and hence XPS is a very surface sensitive technique.

3. Results and discussion

A typical microstructure of OAD grown tungsten nanorods is shown in Fig. 2. As seen in the figure, the nanorods of the size of 25–75 nm diameter are protruding out of the glass substrate at a normal angle are uniformly spread over the glass substrate. The perpendicular growth of tungsten nanorods is more evident on 3D surface topography obtained by atomic force microscopy scanning as shown in Fig. 3. Similar nanorods of Al were also grown on the glass substrate but not shown in the figure. Fig. 4(a)–(d) show the nature of the water droplets on a smooth Al surface, FOTS decorated smooth Al surface (normal sputtering deposition), FOTS decorated Al nanorods (OAD deposited) and FOTS decorated W nanorods (OAD deposited), respectively. While the FOTS coating tends to increase the contact angle to 115° with the water, the roughness of the surface increased the contact angle to 133–134°. Fig. 5(a) and (b) show the presence of the FOTS, on the both W and Al nanorod surfaces, evident by a strong peak of fluorocarbon.

According to the Wenzel model [16], an increase in surface area due to the roughness, can increase the hydrophobicity if $\theta > 90°$, where θ is Young's contact angle. The Wenzel equation states that the apparent contact angle θ^* and roughness factor r (the ratio of actual over apparent surface area) relates by an equation:

$$\cos\theta^* = r\cos\theta \qquad (1)$$

Similarly, according to the Cassie and Baxter law [17], the surface roughness along with low surface energy can create air-gaps that keeps the water droplet floating. This can increase the apparent contact angle of the water droplet on the surface. The relationship between θ^* and fractal surface ϕ_s of the solid on which water droplet sits (the rest on the air in the gap) is given by

$$\cos\theta^* = \phi_s(\cos\theta + 1) - 1 \qquad (2)$$

In addition, the relationship between θ, θ^* and r has been well studied using different models by Lafuma et al. [18]. They discussed different conditions under which the Cassie and Wenzel models can prevail. The contact angles of water on smooth surfaces (the surface roughness is below 1%) obtained by normal sputter deposition in our experiments for Al and W were found to be 51.6° and 36°, respectively. However, OAD deposited films showed much lower contact angle. We tested three different samples of Al with different thicknesses and found that increasing thickness decreases the contact angle. This is due to the increase in the roughness factor with the increase in the height of nanorods. The measured contact angle was below 10° indicating the superhydrophilicity and in accordance with the Wenzel law. Similar results were observed for tungsten nanorods also. The deposition of FOTS on the smooth surfaces of Al and W thin films increased the contact angle dramatically. For FOTS decorated Al

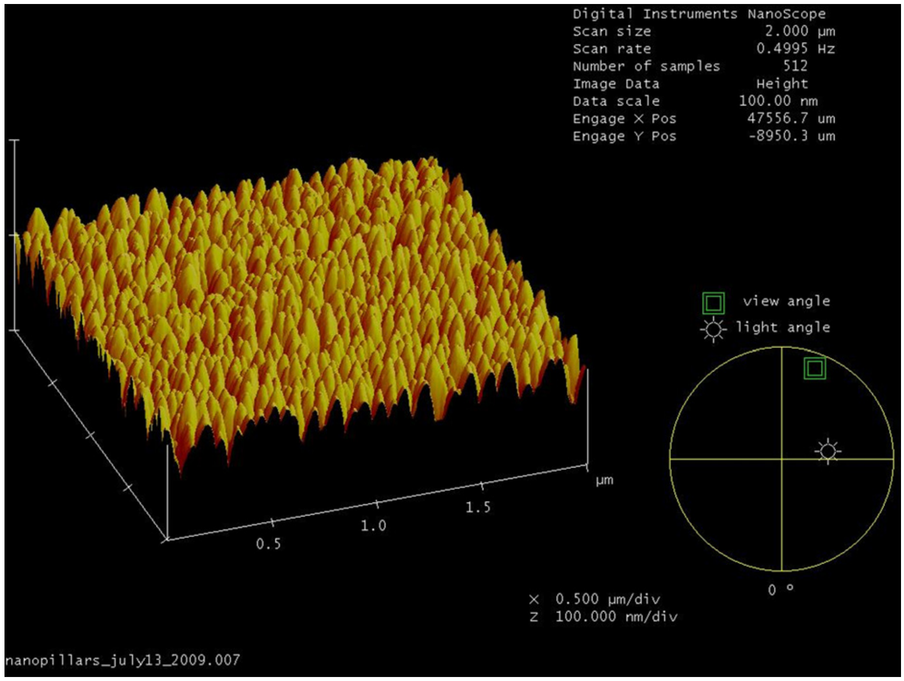

Fig. 3. AFM image of W nanorods grown on a glass substrate.

thin film, the contact angle was 100.2° and for W thin film, it was 100.1°. The contact angle of water on FOTS itself is about 115° (from Gelest Inc. Brochure). However, we observed much lower contact angles with FOTS decorated Al and W thin film surfaces. This may be due to the lack of complete reaction of FOTS with the thin films.

For our further analysis of FOTS decorated nanorods, we consider 100.2° as θ for FOTS decorated Al nanorods and 100.1° as θ for FOTS decorated W nanorods. As mentioned earlier, we tested three samples with different thicknesses for the both Al and W nanorods. The measured contact angles for Al were 107.6°, 110.3° and 134° for 20 min, 30 min and 60 min deposition, respectively.

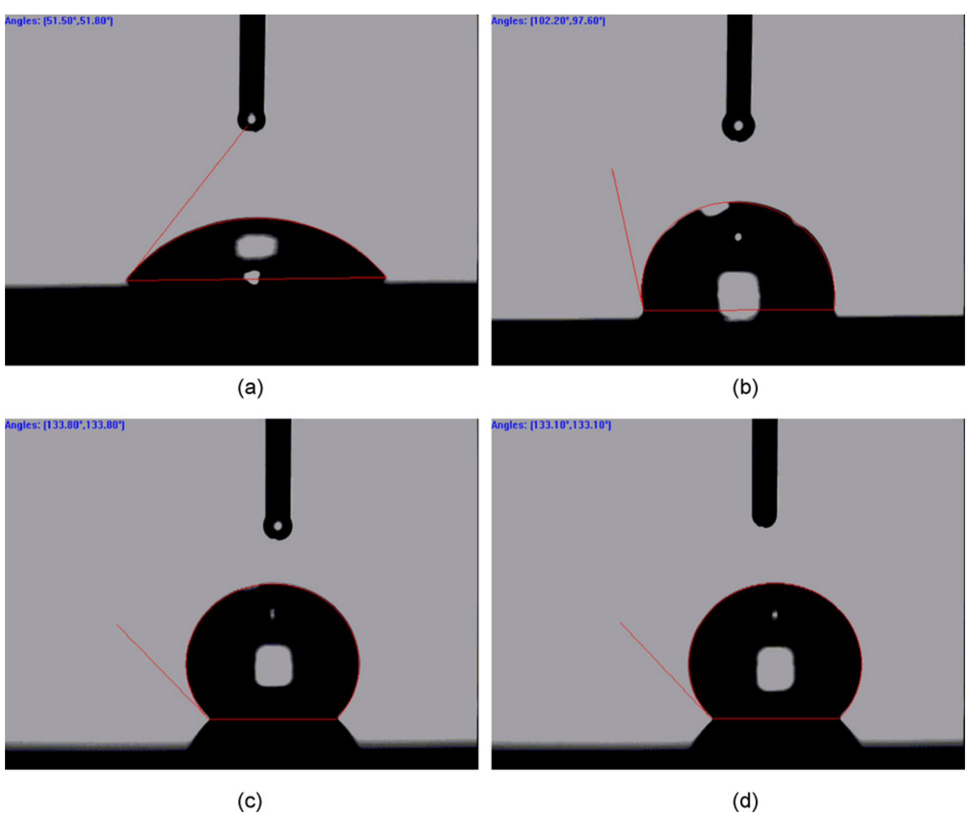

Fig. 4. The shape of water drop on (a) normal deposited Al, (b) FOTS decorated normal deposited Al, (c) FOTS decorated OAD deposited W nanorods, (d) FOTS decorated OAD deposited Al nanorods.

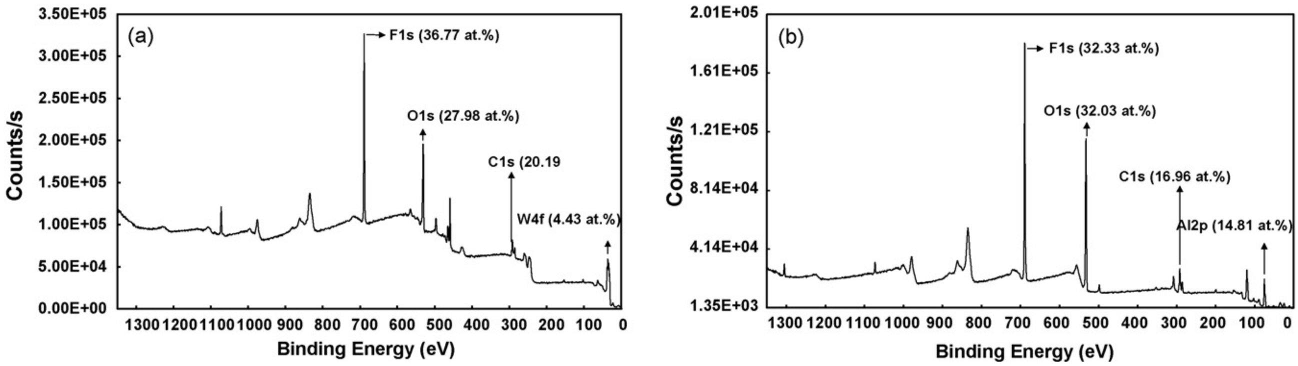

Fig. 5. XPS spectra of FOTS decorated, (a) OAD deposited W nanorods, (b) OAD deposited Al nanorods (for clarity, only the major peaks of interest were labeled).

From the AFM images, we calculated the roughness factor r for all these samples. Using equation 1, we calculated the theoretical Wenzel contact angle. The calculated Wenzel angles for three Al samples were 100.91°, 102.45° and 110.11° for 20 min, 30 min and 60 min samples, respectively. The huge difference between the calculated Wenzel contact angle and the measured contact angles indicate the water droplets were not in the Wenzel state. The other possibility is the Cassie state. However, we could not measure the fractal surface of the solid from the tip of the nanorods from AFM images. So, we are discussing the possibility of Cassie state qualitatively. Hypothetically, with the Wenzel state is ruled out, the water droplet may have in two different conditions. The first one is the Cassie state, obviously due to the low surface energy facilitated by the FOTS and air trapped in the gap that pushes the water drop to the surface. The possibility of existence of the Cassie state with a moderate surface roughness had been reported by several researchers [19–21]. This may be true in our present experiments. However, the apparent contact angles that were measured on our samples are much below than the normal Cassie state could exhibit (above 150°). The second possibility is the co-existence of the Cassie and Wenzel states. We believe the water drop in our sample experienced the co-existence of the Cassie and Wenzel states as explained by the theoretical work from Lafuma et al. [18] (see their models and dotted line in their Fig. 1). In future, we are planning to control the size and gap of nanorods to obtain a higher surface roughness and reduction of surface energy by the silane decoration to achieve contact angles above 150°.

4. Conclusion

In conclusion, we have shown a novel technique of tailoring the metallic surfaces to exhibit hydrophobicity that has the potential in anti-icing applications in aerospace. The probability of water droplets being in the Cassie state on FOTS treated metallic nanorods is encouraging for anti-icing application. The use of sputtering technique ensures a high quality coating with an intense adhesion to the surface. The modification of the surface by the decoration of a monolayer of silane ensures the mechanical properties of the coating are intact.

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References

[1] M. Shi, J. Xi, H. Wang, X. Wu, J. Adhes. Sci. Technol. 22 (2008) 311–318.
[2] M.T. Reetz, Adv. Mater. 9 (1997) 943–954.
[3] D.A. Brevnov, M.J. Barela, M.J. Brooks, G.P. López, P.B. Atanassov, J. Electrochem. Soc. 151 (2004) B484–B489.
[4] T. Kim, C.H. Baek, K.Y. Suh, S. Seo, H.H. Lee, Small 4 (2008) 182–185.
[5] C.W. Sele, T. Von Werne, R.H. Friend, H. Sirringhaus, Adv. Mater. 17 (2005) 997–1001.
[6] X. Fu, X. He, Appl. Surf. Sci. 255 (2008) 1776–1781.
[7] Y. Ofir, B. Samanta, P. Arumugam, V.M. Rotello, Adv. Mater. 19 (2007) 4075–4079.
[8] S. Lee, W. Hwang, J. Micromech. Microeng. 19 (2009) 035019–035023.
[9] L. Chen, M. Chen, H. Zhou, J. Chen, J. Dispersion Sci. Technol. 30 (2009) 48–50.
[10] E. Hosono, Y. Wang, M. Ichihara, H. Zhou, J. Ceram. Soc. Jpn. 117 (2009) 299–301.
[11] Y. Li, Z. Yu, Y. Yu, S. Huo, S. Song, J. Chem. Eng. Chin. Univ. 22 (2008) 6–10.
[12] D.K. Sarkar, M. Farzaneh, R.W. Paynter, Mater. Lett. 62 (2008) 1226–1229.
[13] C. Zhou, D. Gall, Small 4 (2008) 1351–1354.
[14] S.-J. Jiang, C.-Y. Wang, J.-J. Tang, L.-X. Hu, Chin. Phys. Lett. 25 (2008) 4368–4370.
[15] P. Wang, T.C. Parker, T. Karabacak, G Wang, T. Lu, Nanotechnology 20 (2009) 085605–085609.
[16] R.N. Wenzel, Ind. Eng. Chem. 28 (1936) 988–994.
[17] A.B.D. Cassie, S. Baxter, Trans. Faraday Soc. 40 (1944) 546–551.
[18] A. Lafuma, D. Quere, Nat. Mater. 2 (2003) 457–460.
[19] S. Shibuichi, T. Onda, N. Satoh, K. Tsujii, J. Phys. Chem. 100 (1996) 19512–19517.
[20] Z. Yoshimitsu, A. Nakajima, T. Watanabe, K. Hashimoto, Langmuir 18 (2002) 5818–5822.
[21] D. Oner, T.J. McCarthy, Langmuir 16 (2000) 7777–7782.