



# Spray-coating of superhydrophobic aluminum alloys with enhanced mechanical robustness



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## ABSTRACT

A superhydrophobic aluminum alloy was prepared by one-step spray coating of an alcohol solution consisting of hydrophobic silica nanoparticles (15–40 nm) and methyl silicate precursor on etched aluminum alloy with pitted morphology. The as-sprayed metal surface showed a water contact angle of 155° and a roll-off angle of 4°. The coating was subjected to repeated mechanical tests, including high-pressure water jetting, sand particles impacting, and sandpaper shear abrasion. It remained superhydrophobic with a roll-off angle <10° up to three cycles of water jetting (25 kPa for 10 min) and sand particle impinging. After five cycles, the roll-off angle increased, but no more than 19° while the water contact angle remained greater than 150°. The superhydrophobic state was also maintained after three cycles of sandpaper abrasion. It was found that the micro-protrusion structures on the etched aluminum alloy played an important role to enhance the coating mechanical robustness, where the nanoparticles could grab on the rough surface, specifically in the groove structures, in comparison with the smooth glass substrates spray coated with the same materials. Further, we showed that the superhydrophobicity could be restored by spray a new cycle of the nanocomposite solution on the damaged surface.

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## 1. Introduction

Superhydrophobic metals that have water contact angles (CAs) greater than 150° and roll-off angles (RA) below 10° are of wide interests for applications, including anti-corrosion (e.g., inshore and offshore bridge and oil rigs) [1–4], freeze-delay or anti-frost/anti-icing (e.g., air conditioner, refrigerator, antenna, electrical wire, aircraft, and wind power generation system) [5,6], anti-water condensation and heat transfer enhancement [7], anti-fouling [8] and drag reduction for ship's hull [2], and anti-bacteria of medical equipment [9]. There have been extensive efforts to create surface roughness on metals to achieve superhydrophobicity, including chemically etching [10–12], electrochemical an oxidation/deposition [2,13], chemical oxidation/deposition [14,15], and mechanical machining (sandblasting, laser, electrical discharge) [2,14,16]. Nevertheless, the fabricated rough surface can be easily damaged.

For an outdoor environment, it is important that the superhydrophobic metallic surface should survive long-term exposure to water, sand storms and mechanical scratch/abrasion. In particular, to improve the coating robustness against mechanical wear, several strategies have been developed, including crosslinking of the

coating layer [17–19], creation of hierarchical structures [20–22], and introduction of covalent bonds [23,24]. Recently, by depositing cross-linked chitosan and hydrophobic polymers into the nanopores of the alumina, Hohne et al. [25] show that the surface remains superhydrophobic after minor abrasion with a load of ~0.5 N. Boinovich et al. [5] immerse nanoparticles (NPs) and hydrophobic polymer on etched stainless steel to impart superhydrophobicity. The coatings are found durable to cyclic icing/deicing procedure, long-term contact with water and humidity due to the multimodal roughness and bound polymer network. Wang et al. [26] prepare transparent, superhydrophobic coating from polyaniline nanofibers polymerized on the stainless steel surface, followed by fluoro-thiol modification. Superhydrophobicity remains after ultrasonication in water up to 120 min and modest water jetting at a speed of 7.75 m/s. Nevertheless, most of the methods reported in the literature require multiple steps and are limited to relatively small areas. It will be highly desirable to coat the metal substrate in a facial way to achieve superhydrophobicity yet resisting high mechanical force. Further, repeated mechanical abrasion is common in practice. However, few have reported restoration of superhydrophobicity on a damaged surface. In nature, high durability of lotus leaf is achieved through the formation of hierarchical structures [27] and continuously supply of hydrophobic wax layer on the leaf surface [28].

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It has been shown that micro-protrusions that have large bases have higher mechanical stability and less contacting surface area than straight pillars [22]. Therefore, introduction of a second scale nano-roughness on top of and between the micro-protrusions may improve the surface non-wettability with high mechanical robustness. Here, we created superhydrophobic aluminum alloy by first etching the alloy to create rough surface with protrusions and pits, followed by spray coating of an alcohol solution consisting of hydrophobic silica NPs and methyl silicate precursor. The substrates were subjected to several types of mechanical testing, including high-pressure water jetting (10–100 kPa) and the cyclic tests (at 25 kPa), sand particle impacting, and sand paper shear abrasion. The samples maintained superhydrophobicity ( $CA > 150^\circ$  and  $RA < 10^\circ$ ) after all the tests up to three cycles. The water CAs remained  $>150^\circ$  after five cycles of water jetting (25 kPa for 10 min each cycle) and sand impacting, respectively, as well as three cycles of sandpaper abrasion under normal pressure (10 kPa), suggesting that the coating was highly robust. We found that the bonded NPs and their aggregates deposited on the micro-protrusions protected the surface and were responsible for the mechanical robustness. Further, the superhydrophobicity could be regenerated by re-spraying the coating on the damaged surface.

## 2. Experimental section

### 2.1. Materials

All chemicals were used as received. Unpolished aluminum alloys (AA6061, 5 cm  $\times$  76 cm  $\times$  0.6 cm) were purchased from Macmaster-Carr. Hydrophobic fumed silica NPs treated with dimethyldichlorosilane (DDS), AEROSIL™ R972 (A-SiO<sub>2</sub>, Evonik Industries) have an average particle size of 16 nm. Glass resin (GR653L, Technoglas) is an organosilicate precursor with methyl groups. Isopropanol (IPA), hydrochloric acid (HCl), glass slides (1"  $\times$  3") and sea sands (10–300  $\mu$ m in diameter) for testing resistance to sand abrasion were purchased from Fisher Scientific.

### 2.2. Fabrication of micro-protrusions on aluminum alloy

The aluminum alloy substrates (2.4 cm  $\times$  3.2 cm  $\times$  0.6 cm) were pre-cleaned by sonication in acetone and ethanol for 20 min, respectively. After drying, the substrates were chemically etched by 15 vol% HCl aq. for 45 min, followed by rinsing under running water, sonication in acetone, ethanol and distilled water for 30 min, respectively, until no more reaction was found in the solvent. Finally, the substrates were dried in an oven at 65 °C for 10 min.

### 2.3. Spray-coating of nanoparticle/resin composite

A-SiO<sub>2</sub> and GR653L were first dispersed in IPA separately and sonicated for 15 min before mixing together at 1:1 v/v. The mixture was sonicated for another 15 min before use. The A-SiO<sub>2</sub> NP/ GR653L composites were referred as nanoparticle composite (NPC). Their suspension in alcohol was continuously sprayed on the etched aluminum alloy substrates in a line-to-line fashion for eight cycles using an airbrush under compressed air (20 psig working pressure) at room temperature with a moving speed of 2–5 cm/s. A typical distance of 5–15 cm was used in the experiments. There was no post-treatment of the samples. For comparison, solutions with NPs only and glass resin only were also spray-coated on the substrates.

### 2.4. Wettability and surface morphology

The water CAs of the samples were measured by Ramé-Hart standard automated goniometer (Model 290). The static water CA was measured from a 5.0  $\mu$ L deionized water droplet and averaged over three different fresh spots on each sample. Advancing and receding water CAs were measured by automatically adding and removing water from the substrate, respectively. For roll-off angle (RA) measurement, the substrate was placed on a custom-designed stage attached with a protractor and a 10  $\mu$ L water droplet was used. All RA values were averaged over three different measurements on each sample. The morphologies of the substrates, which were sputter-coated with gold, were imaged with an FEI Quanta 600 FEG environmental scanning electron microscopy (ESEM) at an acceleration voltage of 30 kV.

### 2.5. Mechanical testing

Mechanical resistance of the substrates was evaluated by sand impacting, high-pressure water jetting, and sand paper abrasion. The continuous water jetting apparatus was homebuilt as shown in Fig. S1a. The samples were fixed on a substrate tilted at 45° and placed 5 cm below a water pipe (inner diameter, 4 mm), and then jetted for 10 min at different pressures (10–100 kPa). The films were water jetted at 25 kPa repeatedly up to five times to investigate the cyclic durability. For sand impacting tests,  $\sim$ 10 g sea sands were dropped onto the tilted substrate surface (tilt angle  $\alpha = 45^\circ$ ) in 1 min from a height of 30 cm above the substrate (Fig. S1b). To evaluate shear abrasion (Fig. S1c), Emery polishing paper (9  $\times$  13–3/4 and 2000 Grit (GRADE 4/0 from Behr-Manning Co.) was used. While a pressure (10 kPa) was applied normal to the sand paper, the substrate was moved in one direction with a speed of 6 cm/s for 30 cm. The tests were repeated five times on the surface, and the water CAs and RAs were measured after each test.

## 3. Results and discussion

The fabrication of superhydrophobic aluminum alloys is illustrated in Fig. 1. It included two-step processes to create multimodal roughness, including chemical etching by HCl aq. to produce pitted structures and subsequent spray coating of NPCs dispersed in IPA, consisting of A-SiO<sub>2</sub> NPs and glass resin precursor, GR653L.

To achieve superhydrophobicity, it is essential to have a uniform and complete surface coverage of the NPC coating. The assembly of hydrophobic NPs provides both the surface hydrophobicity and the surface roughness. Meanwhile, glass resin offers binding between the NPs and NP and the substrate. However, too much glass resin could embed the NPs, decreasing surface roughness. Therefore, it will be necessary to carefully tune the concentration of each ingredient and their spray cycles. When the concentration of A-SiO<sub>2</sub> was low ( $<2$  mg/mL, concentration of GR653L = 2 mg/mL, Fig. 2a), the surface coverage of the NPCs was insufficient to achieve superhydrophobicity if the number of spraying cycles was less than eight. At a higher concentration of A-SiO<sub>2</sub> (e.g.  $>10$  mg/mL), the surface coverage was improved, however, there was not sufficient GR653L to bind hydrophobic NPs. Therefore, we fixed the concentration of A-SiO<sub>2</sub> at 5 mg/mL, but varied the concentration of GR653L. Similarly, superhydrophobicity could not be achieved if the concentration of GR653L was lower than 2 mg/mL or higher than 8 mg/mL (Fig. 2b). For the study reported here, we fixed the concentrations of A-SiO<sub>2</sub> and GR653L to be 5 mg/mL and 2 mg/mL, respectively. Water CAs  $>150^\circ$  could be achieved on the coated glass after spraying three cycles or more, although RAs remained high ( $>20^\circ$ ) until the spraying coating cycle

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