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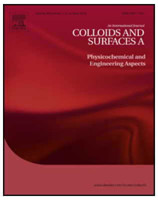

Spray-coated superhydrophobic surfaces with wear-resistance, drag-reduction and anti-corrosion properties

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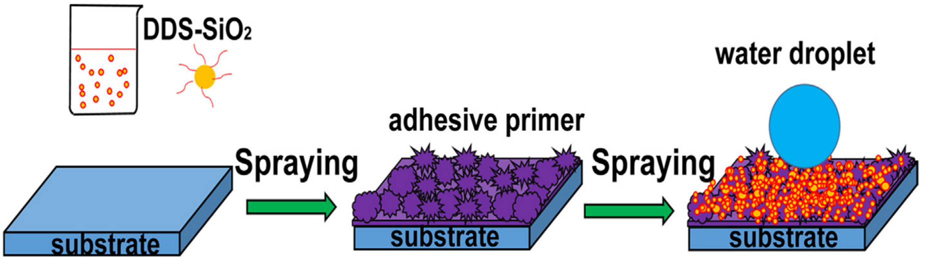
HIGHLIGHTS

- The superhydrophobic surfaces are fabricated with a facile two-step spraying method.
- Excellent superhydrophobicity with high water contact angle and low sliding angle is obtained.
- The as-prepared surfaces show good mechanical durability, anti-corrosion and drag reduction properties.
- The fabrication method is simple and suitable for industrial process in a large scale.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper proposes a facile and low-cost method of preparing superhydrophobic surfaces on aluminium substrates using a two-step spraying method. A layer of hydrocarbon resin adhesive was sprayed on the substrate, after which dichlorodimethylsilane-modified hydrophobic silica nanoparticles were sprayed on the adhesive primer. The surface morphology, wettability and chemical composition were characterized by scanning electron microscope, water contact angle meter and X-ray photoelectron spectroscopy, respectively. The water contact angle of the superhydrophobic surface reached $153.5^\circ \pm 1.5^\circ$ and the sliding angle was $1.8^\circ \pm 0.2^\circ$. The surface exhibited good wear-resistance in sandpaper abrasion, finger-wiping and knife-scratching tests. Even if damaged, the surfaces could be easily repaired. Rheometry results showed that the surface drag reduction rate reached up to 48.7%. Dynamic polarization tests indicated a great improvement in anti-corrosion properties with a decrease of two orders of magnitude in the corrosion current. The present method can be easily expanded to other materials and does not require special conditions, advanced equipment or complicated preparation processes, making it suitable for mass production.

1. Introduction

Superhydrophobic surfaces, which are water-repellent surfaces with a water static contact angle larger than 150° and a sliding contact angle lower than 10°, have attracted wide attention in scientific research and engineering [1–4]. They have useful applications in many areas owing to their unique non-wetting property, such as self-cleaning [5], anti-corrosion [6,7], anti-icing [8], oil and water separation [9] and drag reduction [10–12], and are expected to bring about huge breakthroughs in construction, environmental protection, marine, energy conservation, smart devices, microfluidics and other fields.

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A variety of methods have been employed successfully to prepare superhydrophobic surfaces, such as chemical vapour deposition [13], chemical/electrochemical etching [14–16], laser etching [17,18], sol-gel methods [19], sintering [20], and dip-coating [21]. However, these methods generally require specific experimental conditions, a long preparation period, complicated processes and strict restrictions on the shape of the substrate, so they are unable to meet the requirements of practical applications [22]. Therefore, simple, time-saving and low-cost fabrication methods are needed. In contrast to the above methods, spraying only requires a spray gun and an air pump, and does not demand special experimental conditions or complex operations, and has no restrictions on substrate shape and size. Thus, it is an ideal method [4,23]. There have been some reports in the literature on the use of spraying methods to prepare superhydrophobic surfaces. Ogihara et al. [24] sprayed a nanoparticle suspension directly on to the surface of a fibrous substrate, followed by low surface-energy modification. For fibrous substrates and other porous materials, nanoparticles can be attached to the inner wall of fibre pores to be protected. But for aluminium, steel and other bulk materials, the stable adhesion of nanoparticles to the substrate surface cannot be guaranteed using this method. Jung et al. [25] mixed organic resin, carbon nanotubes, and surface modifying agents in an organic solvent and then sprayed the mixture on an Si surface. Although organic resin can enhance the adhesion of a nano-coating with the substrate surface, but organic resin coats the nanoparticles, resulting in them only serving as building blocks of the surface multiscale structures. The organic resin is in contact with the droplets and requires additional surface modifying agents. However, not all organic resin can be modified with low surface-energy materials, so there are some limitations in the choice of organic resin.

Superhydrophobic surfaces face the problem of poor mechanical durability, which is main factor impeding their practical applications [26–28]. The hierarchical surface structures formed by micro-nano assemblies have poor mechanical durability because of the weak adhesion between the hierarchical structures and the substrate, especially for nanoscale structures. If the adhesion between the substrate and surface nanoscale structures can be enhanced, the mechanical durability of the surface will increase. The sintering method has been reported to enhance the adhesion between nanostructures and substrates [29], but the high temperatures used in the sintering process are not suitable for some substrates, such as plastics and polymer films. Adhesives can strengthen the adhesion between surface structures and substrate and thereby stabilize fragile superhydrophobic surfaces. Lu et al. [30], joined substrates nano-coating with double-sided adhesive tape and obtained enhanced mechanical stability. However, double-sided adhesive tape has certain limitations regarding substrate size and shape, and cannot easily be used for large-area coating of non-planar surfaces. Verho et al. [31] proposed that the mechanical stability of the surface could be enhanced by protecting the nanoscale structures with microscale structures. Zimmermann et al. [32] grew a layer of polymethylsilsesquioxane nanofilaments on textile fibres to fabricate hierarchical superhydrophobic fibres. Although some of the external nanofilaments on the contact surfaces were worn away under a force of 5 N, they remained intact in other parts, and the fibres maintained their superhydrophobic character. Kondrashov et al. [33] prepared a robust superhydrophobic surface with microcones and nanograsses on silicon. Exposed to varying shear loads, the microcones served as pillars that endured the brunt of the high pressure and protected the nanostructures from being worn. The above methods were based on the design idea of protecting fragile nanostructures with strong microstructures.

In this paper, a simple, low-cost and effective spraying method is reported for the preparation of superhydrophobic surfaces on aluminium substrates. A layer of hydrocarbon resin adhesive was sprayed onto the substrate, followed by spraying of a layer of hydrophobic silica nanoparticles. The as-prepared surfaces exhibited excellent superhydrophobic characteristics and good mechanical durability during sandpaper abrasion, finger-wiping and knife-scratching tests. Even if the surfaces were damaged under long periods of abrasion, they could be easily repaired. Rheometry and dynamic polarization measurements were used to confirm the excellent drag reduction and anti-corrosion properties of the superhydrophobic surfaces. Compared with other preparation methods, this method is simpler, cheaper and not limited by the material or shape of the substrate. Moreover, it has the advantage of easy repair, and is expected to accelerate the practical applications of superhydrophobic surfaces.

2. Experimental

2.1. Materials

$30 \times 30 \times 0.3\,\text{mm}^3$ aluminium sheets (99.9%) were purchased from Shenzhen Oudifu Metal Material Co. Ltd, China. The sheets were cleaned successively with ultrasonication, using acetone, anhydrous ethanol and deionized water for 10 min each, and then dried with compressed air. DDS-SiO_2 nanoparticles were purchased from Evonik Inc, Germany. These hydrophobic silica nanoparticles were modified with dichlorodimethylsilane (DDS), and had an average particle diameter of about 16 nm. Hydrocarbon resin adhesive was purchased from Rust-Oleum Co. Ltd, USA. All chemicals were used as received without further processing.

2.2. Fabrication of superhydrophobic surfaces with spraying method

Initially, a 4 wt% ethanol suspension of silica nanoparticles was prepared. The hydrophobic nanoparticles were added to anhydrous ethanol and ultrasonication was used to distribute the nanoparticles uniformly in the suspension. A schematic diagram illustrating the preparation of the superhydrophobic surface with a two-step spraying method is shown in Fig. 1. First, a layer of hydrocarbon resin adhesive was sprayed on the clean substrate surface, and repeated 2 or 3 times. Each time lasted 5 s with an interval of 3 min. Next, the prepared silica ethanol suspension was sprayed onto the primer for 10 s 5 times, with an interval of more than 60 s to ensure sufficient evaporation of the ethanol. After curving for 24 h at room temperature, robust superhydrophobic surfaces were obtained.

2.3. Characterization

Water contact angles (CAs) and sliding angles (SAs) were measured with a contact angle meter (JC2000D, China), using 10 μL droplets at room temperature. The surface morphology of the samples was observed by scanning electron microscope (SEM, Sirion 200, FEI) at different magnifications. Before SEM observation, a very thin gold (Au) layer was sprayed on the sample to enhance its conductivity. The surface chemical compositions were analysed by X-ray photoelectron spectroscopy(XPS, ESCALAB 250Xi, Thermo Fisher) with a monochromatic Kα source. Sandpaper abrasion, finger-wiping and knife-scratching tests were used to study the wear-resistance properties of the as-prepared surfaces. Friction torques at different rotating speeds were measured with a standard parallel-plate rheometer (Physica MCR301, Aaton Paar) to verify the drag reduction effect. Potentiodynamic polarization tests were conducted to analyse the anti-corrosion property, using an electrochemical workstation (CHI660E, China) in a 3.5 wt% NaCl aqueous solution, imitating the corrosive environment of seawater. The as-prepared sample served as a working electrode, while a platinum