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Atomised spray plasma deposition of hierarchical superhydrophobic nanocomposite surfaces

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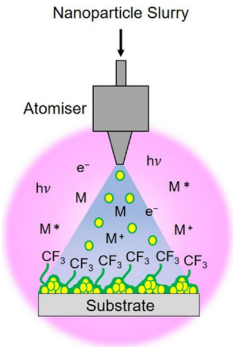
GRAPHICAL ABSTRACT



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ABSTRACT

Atomised spray plasma deposition (ASPD) using perfluorotributylamine–nanoparticle slurry mixtures yields superhydrophobic nanocomposite layers in a single solventless step. X-ray photoelectron and infrared spectroscopies indicate the formation of a poly(perfluorocarbon) host matrix containing nanoparticles. Electron microscopy shows the appearance of hierarchical surface roughness through the incorporation of nanoparticles. This gives rise to a synergistic effect combining low surface perfluoroalkyl groups and surface roughness leading to enhanced water and oil (hexadecane) contact angle values. Microindentation measurements show that the mechanical properties of the deposited liquid repellent nanocomposite layer are enhanced through the incorporation of methacryloyl functionalised silica, zinc oxide, or graphene nanoparticles.

1. Introduction

Liquid repellent surfaces have attracted significant interest for societal and industrial applications, including: self-cleaning [1], anti-icing [2], anti-fogging [3], building materials [4], electronic devices [5], antifouling [6], anti-corrosion [7], antibacterial [8], drag reduction [9], oil–water separation [10,11], and anti-thrombotic surfaces [12]. One approach for attaining hydrophobicity is inspired by the water repellency properties of the lotus leaf (*Nelumbo nucifera*)—which contains microscale surface bumps (papillose epidermal cells) covered by nanoscale epicuticular waxes [13]. This hierarchical roughness reduces the solid–liquid contact line by increasing the liquid–air contact line due to entrapped air pockets at the composite solid–liquid–air interface, thereby facilitating the movement of droplets along the plant leaf surface leading to self-cleaning [14].

A combination of such hierarchical roughness with low surface energy materials for the preparation of superhydrophobic surfaces has been reported in the past by fabrication methods such as:

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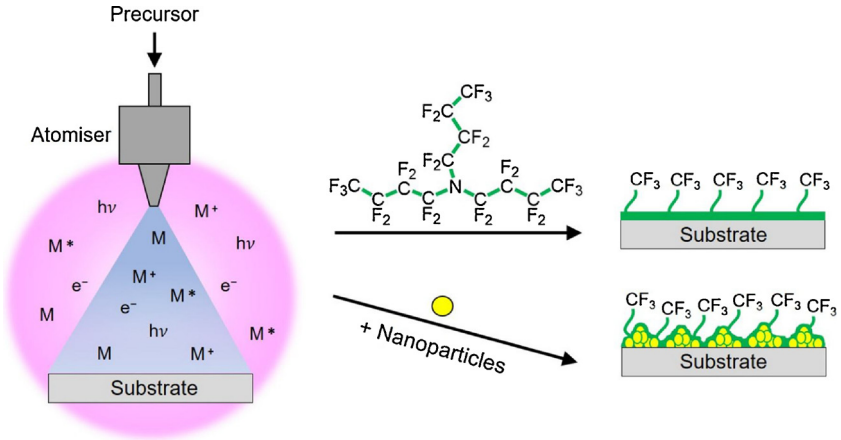

Scheme 1. Atomised spray plasma deposition (ASPD) of perfluorotributylamine–nanoparticle nanocomposite layer.

photopolymerisation [1], spray casting [15], electrodeposition [16], hydrothermal process [9], chemical vapour deposition [17], plasma polymerisation [18], sol-gel [19], electrowetting [20], layer-by-layer [21,22], dip coating [23], lithography [24], fluorination [25], and etching [26]. However, many of these techniques suffer from limitations, including: solvents [15,27], multi-step [17,19,28], lengthy [3], requiring high vapour pressure precursors [29], post-heat treatments [4], poor adhesion [30], etc.

In this article, we describe an approach which overcomes the aforementioned disadvantages. This comprises the single-step atomised spray plasma deposition (ASPD) of liquid repellent nanocomposite coatings using a low surface energy precursor–nanoparticle slurry (perfluorotributylamine mixed with methacryloyl functionalised silica, zinc oxide, or graphene nanoparticles), which yields hierarchical roughness and mechanical hardness, Scheme 1. The selection of a fluorocarbon precursor provides for both water and oil repellency, and the utilisation of a sub-atmospheric pressure plasma avoids the requirement for expensive carrier gases as well as providing the safe removal of volatile toxic low molecular by-product species [31].

2. Experimental

2.1. Atomised spray plasma deposition

Precursor materials used were perfluorotributylamine (+99.9%, Fluorinert FC-43, 3M Inc.), and a variety of nanoparticles: methacryloyl functionalised silica nanoparticles (12 nm primary particle size and 100–200 nm average aggregate size, Aerosil R711®, Evonik Industries AG); zinc oxide nanoparticles (< 100 nm particle size, Sigma-Aldrich Ltd.); and graphene nanoplatelets (2–10 nm thickness and < 2 µm particle diameter, Strem Chemicals UK Ltd.). Unfunctionalised silica nanoparticles display hydrophilic behaviour due to surface hydroxyl groups, and were found not to readily disperse in low surface tension liquids (e.g. perfluorotributylamine). Instead, methacryloyl functionalised SiO_2 nanoparticles (methacryloyl-SiO_2) were used due to their ease of dispersion in non-polar liquids [32]. For the case of perfluorotributylamine precursor mixed with methacryloyl functionalised silica and zinc oxide nanoparticles (ratio 1:1 w/w), 5% v/v of trifluoroacetic acid (+99%, Fluorochem Ltd.) was added to improve dispersion (carboxylic acid groups can interact with ZnO surfaces) [33,34]. Liquid monomer–nanoparticle mixtures were sonicated for 45–60 min to fully disperse the nanoparticles (Clifton ultrasonic bath, Nickel-Electro Ltd.), and then loaded into a sealable glass delivery tube. This precursor slurry mixture was then degassed using several freeze–pump–thaw cycles. Substrates used for coating were glass microscope slides (Academy Science Ltd.) and silicon (100) wafers (0.014–0.024 Ω cm resistivity, Silicon Valley Microelectronics Inc.). These were cleaned in three steps: ultrasonicated in a 1:1 v/v mixture of propan-2-ol (+99.5 wt %, Fisher Scientific Ltd.)/cyclohexane (+99.7%, Sigma-Aldrich Ltd.) for 5 min and air dried, followed by UV ozone cleaning (ProCleaner model UV.TC.EU.003, BioForce Nanosciences Inc.) for 10 min, and finally ultrasonicated in a 1:1 v/v solvent mixture of propan-2-ol/cyclohexane for 5 min followed by air drying before placement downstream in line-of-sight from the atomiser, Fig. 1.

Atomised spray plasma deposition was carried out in an electrodeless, cylindrical, T-shape glass reactor (volume 1117 cm^3, base pressure of 3×10^{-3} mbar, and a leak rate better than 2×10^{-9} mol s^{-1}) [35] enclosed in a Faraday cage. The chamber was pumped by a 30 L min^{-1} two-stage rotary pump (model E2M2, Edwards Vacuum Ltd.) attached to a liquid nitrogen cold trap, and the system pressure monitored by a thermocouple gauge. An L–C impedance matching network was used to minimise the standing wave ratio for power transmitted from a 13.56 MHz radio frequency (RF) power supply to a copper coil (4 mm diameter, 7 turns) located downstream from an atomiser (20 µm diameter median droplet size [36,37], model No. 8700-120, Sono-Tek Corp.), which was driven by a broadband ultrasonic generator (120 kHz, model No. 06-05108, Sono-Tek Corp.). Prior to each deposition, the chamber was scrubbed with detergent, rinsed with propan-2-ol and acetone (+99%, Fisher Scientific Ltd.), and oven dried. Next, a continuous wave air plasma was run at 0.2 mbar pressure and 50 W power for 30 min to remove any remaining trace contaminants from the chamber walls. Ambient temperature deposition was carried out using a 30 W continuous wave plasma in conjunction with atomisation of the solid–liquid slurry into the reaction chamber employing an optimised flow rate of $16 \pm 4 \times 10^{-4}$ mL s^{-1} (higher flow rates produce unstable films due to incomplete polymerisation). Upon plasma extinction, the atomiser was switched off and the system was evacuated to base pressure, followed by venting to atmosphere. The chemical stability of the deposited nanocomposite layers towards polar and non-

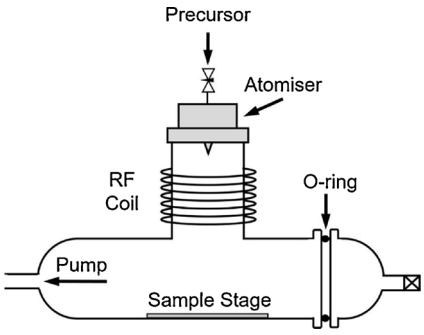

Fig. 1. Atomised spray plasma deposition (ASPD) chamber.