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Hierarchical surface coatings of polystyrene nanofibers and silica microparticles with rose petal wetting properties

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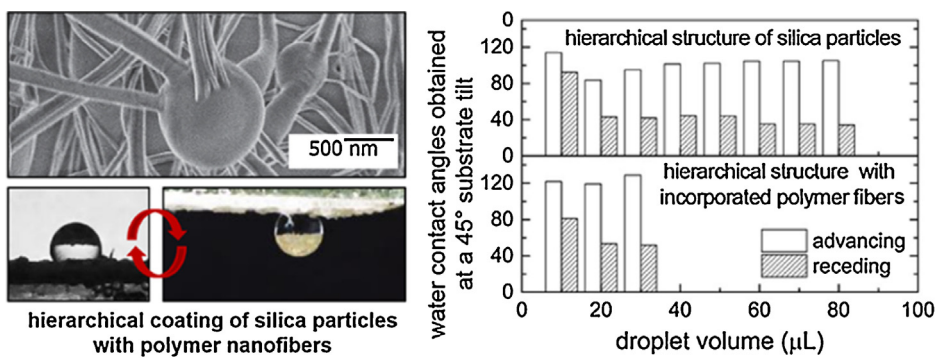
HIGHLIGHTS

- Hydrophobic surfaces with high water adhesion were prepared by simultaneously spray coating a polystyrene binder and silica particles.
- A hierarchical structure with decreasing size of silica particles was created by tuning the composition of the spray coating suspension.
- The resulting hierarchical structure also contained ~100-nm diameter polystyrene nanofibers that interlaced throughout the coating.
- The hydrophobicity of these surfaces was tuned by incorporating a combination of microscale to nanoscale structures.
- The structured coatings were able to more efficiently condense water vapor under low humidity, yet, retained minimal water at high humidity.

GRAPHICAL ABSTRACT



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ABSTRACT

Surfaces with rose petal like properties, simultaneously exhibiting a high degree of hydrophobicity and a high adhesion to water, were prepared by spray coating of progressively smaller hydrophilic silica particles along with hydrophobic nanofibers onto surfaces of interest. Various polymer structures were achieved by tuning the spray coating flow rates during deposition of the polymer nanofibers and silica particles. At a reduced flow rate, polystyrene fibers were formed with diameters of less than 100 nm. Water contact angles (WCAs) of coatings prepared from the hierarchical assemblies of silica particles blended with polystyrene nanofibers were greater than 110°. Coatings prepared from the hierarchical assemblies either with or without incorporation of the polymer nanofibers pinned water droplets to their surfaces even after inverting the substrates, similar to the properties of a rose petal. Hierarchical coatings

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of silica particles without the polystyrene nanofibers also exhibited a high adhesion to water, pinning at least 30% more water on its surfaces. Conversely, hierarchical coatings containing the polystyrene nanofibers exhibited an increased water mobility across their surfaces. Further water retention experiments were performed to determine the ability of the different coatings to efficiently condense water vapor, as well as their efficiency to remove this condensed liquid from their surfaces. Both types of hierarchical coatings exhibited an excellent ability to retain water at a low humidity, while establishing a self-limiting condition for retaining water at a high humidity. These coatings could be prepared on a relatively large-scale and with a relatively low cost on the surfaces of a variety of materials to enhance their water resistance, water retention and/or ability to condense water vapor.

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1. Introduction

One of the more interesting characteristics of microstructured surface textures observed in nature are those of rose petals. The surfaces of rose petals exhibit a strong hydrophobicity, while simultaneously displaying a high adhesion to water droplets even when the surfaces are inverted by 180°. Rose petal surfaces contain distinct features with dimensions that can be classified on at least two different scales [1–13]. The hierarchical roughness of these surfaces enables water droplets to penetrate into the void spaces between the larger, microscale structures while limiting further wetting and penetration of water into the surfaces with the inclusion of nanoscale hydrophobic features [3–9]. The wetting properties of rose petal surface is a delicate balance between the Cassie-Baxter state [14] — where a water droplet is supported on surfaces with entrapped air pockets — and the Wenzel state [15] — where a water droplet is fully wetting the surfaces.

The wetting properties of microstructured surfaces are of widespread interest for their self-cleaning [16–18], anti-reflection [19,20], and fluid drag reduction [21] properties. These characteristics of surface coatings can be achieved through chemical modifications [22,23] and/or the addition of microstructures [6–10,24,25]. Many natural biological materials, such as lotus leaves [26], water strider legs [27], and avian feathers [28,29], possess specialized water repelling surfaces. Variations in surface micro- and nanostructures can further transform hydrophobic surfaces into adhesive materials that have similar properties and structures as a gecko's foot [30,31], and a spider's leg [32].

Applications in creating surfaces with an enhanced water resistance, improved capability of collecting water, and/or proficiency in maintaining moisture has inspired many researchers to prepare rose petal-like surfaces. Many studies have demonstrated that the opposing water wetting states, namely hydrophobicity and hydrophilicity, of surfaces can be tuned by varying the dimensions of micro- and nanostructures [2–12]. One method for preparing surfaces with well-defined structures uses reactive ion etching to prepare regular arrays of cylindrical silicon nanopillars [12]. By tuning the reaction conditions, silicon protrusions can be created with conical or pyramidal asperities and average heights of ~10 micrometers and can be further tuned to mimic hierarchical structures [33]. Structured surfaces prepared by this semiconductor fabrication process can achieve very high water contact angles (WCAs) of ~150°, and exhibit a high adhesion for water droplets even when the substrate was inverted. Nanoimprint lithography has also been used to prepare surfaces with the desired water wetting and adhesion properties. Some examples include the use of biological templates and nanoimprint lithography with lotus leaves, butterfly wings, and rose petals [34–37]. However, each of these techniques is relatively expensive due to the required equipment. To reduce costs, researchers have used relatively inexpensive materials, such as vapor deposited polystyrene nanopillars [38], parylene nanofibrillar structures [39], plasma etched and structured polydimethylsiloxane films [40], hydrothermally deposited antimony oxide films [41], and zinc oxide nanorods [42] to mimic rose petal-like surfaces. Although these methods are relatively inexpensive, the surface areas coated by each process are still limited by equipment constraints. For example, the size of the chambers for vapor deposition or plasma etching will ultimately limit the maximum dimensions of the coated surfaces. There are still further challenges to apply these methods and materials to modifying larger areas and other surfaces, such as the exteriors of buildings or interior walls, for the purposes of managing water retention and transport.

In this study, we pursue a relatively inexpensive method for preparing rose petal inspired surfaces. A simple and quick method was developed to prepare coatings on a variety of substrates that combined spray coating of silica particles with the simultaneous formation of nanofibers from a polystyrene binder. These spray coating techniques could be extended to prepare coatings that cover relatively large areas. Coatings were prepared in a layer-by-layer fashion with a decreasing size of silica particles with increasing thickness. These hierarchically assembled coatings of silica particles with the inclusion of polymer nanofibers exhibited a large WCA hysteresis that is a distinguishing characteristic of rose petal surfaces. By tuning the conditions for deposition of the silica particles and polymer binder, the surface topographies were further tuned to increase or decrease their hydrophobicity while retaining a relatively high adhesion to water when inverted. Through the development of the techniques outlined in this study, rose petal inspired surfaces for potential use in interior or exterior environments could be pursued on a relatively large scale as required for a variety of applications in the management of water adhesion and/or transport.

2. Materials and methods

2.1. Preparation of structured surfaces

Two types of silica particles, smaller particles (200 mesh particles with measured diameters between 1 and 250 μm) and larger particles (40 mesh particles with measured diameters below 500 μm), were purchased from Mallinckrodt Silica AR® and B. Braun Melsungen AG, respectively. Polystyrene (45,000 M.W.) that was used as a binding agent for these silica particles was purchased from Sigma-Aldrich. These materials were spray coated using an airbrush coater (Crescendo 175®) purchased from Badger Air-Brush Company. All solvents used in this study were purchased from Sigma-Aldrich. The solutions prepared for spray coating contained mixtures of silica particles and polystyrene binder suspended in toluene. These mixtures were deposited by spray coating onto flat glass substrates from a distance of 30 cm while tuning the air flow parameters (with ranges tuned between 2.4 and 12 mL/min) to achieve different surface topographies. Glass microscope slides were chosen as the test substrate for these studies

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