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Full Length Article

# Design of water-repellant coating using dual scale size of hybrid silica nanoparticles on polymer surface

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ABSTRACT

The dual-scale size of the silica nanoparticles is commonly aimed at producing dual-scale roughness, also called hierarchical roughness (Lotus effect). In this study, we describe a method to build a stable water-repellant coating with controlled roughness. Hybrid silica nanoparticles are self-assembled over a polymeric surface by alternating consecutive layers. Each one uses homogenously distributed silica nanoparticles of a particular size. The effect of the nanoparticle size of the first layer on the final roughness of the coating is studied. The first layer enables to adjust the distance between the silica nanoparticles of the upper layer, leading to a tuneable and controlled final roughness. An optimal size nanoparticle has been found for higher water-repellency. Furthermore, the stability of the coating on polymeric surface (Polycarbonate substrate) is ensured by photopolymerization of hybridized silica nanoparticles using Vinyl functional groups.



## 1. Introduction

Superhydrophobic surfaces obtained by combining surface roughness with lower surface energy have attracted the interest of both fundamental scientists and the industrial community due to the unique properties. Inspired by nature (e.g. Lotus leaves, insect legs and insect wings), a wide range of applications of superhydrophobic surfaces have emerged such as self-cleaning windows or solar panels [1,2] and anti-corrosion coating [3]. Superhydrophobic coatings have been developed using various methods such as electroless depositions [4], spray-coating processes [5,6], the sol-gel method [7], laser-ablation [8] and electrospinning [9].

Chemical modifications of a smooth surface by grafting hydrophobic molecules modify the surface energy leading to a hydrophobic surface, with a contact angle up to 90°. Inducing a roughness at the surface strongly affects the wetting and significantly improves the apparent contact angle (>90°). Increasing the roughness leads to a superhydrophobic surface with a contact angle >150° [10]. The superhydrophobic feature was described by Wenzel [11] and Cassie-Baxter [12] models. The Wenzel model assumes that the contact between the water droplet and the surface of the solid occurs everywhere, whereas the Cassie-Baxter models describes a composite (solid-liquid-air) surface where the water droplet is suspended by top elements of the surface and the scavenged air reduces the surface contact. Although these two models are subject to criticism [13,14], they remain the fundamental models which describe the wetting of structured surfaces. These models provide mechanisms to understand how roughness can affect the static contact angle when the water drop is sitting on a rough surface, but they do not allow to predict hysteresis [15].

Hierarchical structures with a dual-scale roughness, or more, have been reported as an efficient nanostructure to achieve low contact angle hysteresis with high contact angle. This composite surface with air pockets in the valleys between asperities reduces the solid-liquid contact area. The combination of micro-sized papillose epidermal cells with nano-sized tubules at the surface of the Lotus leaf is one among many living examples that show the efficiency of combining such different scales. Silica nanoparticles obtained using a Stöber soft chemistry [16] with a controllable size are suggested to control the surface roughness in the nano- and micro-scale. Recent studies showed the use of nanoparticles aggregation to create both microscale and nanoscale roughnesses leading to a hierarchical structure [5,17]. Others reported the beneficial effect of combining two variable sizes of silica nanoparticles, in order to create dual-scale roughness for robust Cassie state of wetting [18,19]. Indeed, hierarchical roughness is required for the system stability and the robustness of the liquid repellent surfaces by increasing the breakthrough pressure of the liquid droplets

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[20,21]. Although the results show a synergetic effect, there is a contrast with existing literature suggesting that the randomly distributed monoscale nanoparticles and moderately dense coverage of the surface enable to achieve superhydrophobic properties [22]. The surface roughness decreases when increasing the coverage of the surface. The low density coverage of the substrate provides the desired distance between the silica nanoparticles, leading to an increase of the root-mean-square (rms) roughness, unfortunately with moderate control. A theoretical study performed by De Coninck and coworkers led to a similar conclusion [23]. The authors showed that the free energies and contact angles depend mostly on the density of nanoparticle distributed all over the surface. However, introducing a disordered nanoparticle distribution in a periodic substrate could lower the contact angle, and the disordered substrate will have a lower contact angle relatively to an ordered one.

Many studies reported the elaboration of superhydrophobic coating (using $SiO_2$ nanoparticles) on glass substrates [2,5,18,22]. The consolidation of the nanoparticles on a glass substrate is much easier, since the sintering process is usually used at high temperatures. However, the elaboration of superhydrophobic coating on a heat-sensitive polymer substrate is scarcely studied. The immobilization of nanoparticles needs to be performed at a low temperature because of their thermo-sensitive nature, and wettability/adhesion (due to low surface free energy). Therefore, the stabilization of silica nanoparticles remains a challenge.

In this study, we describe a strategy to design stable water-repellant coating made by hybrid silica nanoparticles on polymer substrates. The coating is the stack of two layers. Hybrid silica nanoparticles allowing the formation of bonds to stabilize the coating at low temperatures on the polymeric surface form the first layer. The nanoparticles' sizes are controlled in the range of 40 nm to 150 nm. Thus, we were able to control the density of the second layer of silica nanoparticles as well as the distance between them, previously reported as limiting parameters.

## 2. Experimental section

### 2.1. Coating design

The water-repellant coating consisted of two layers intended to control the roughness (Fig. 1a). The first layer (in contact with the substrate) was elaborated using a well-controlled size of hybrid silica nanoparticles. Tuning the size of the silica nanoparticles enabled to control the distance between the nanoparticles in the top layer (where the size used is fixed at 100 nm) and consequently control the roughness. As illustrated in Fig. 1b, each nanoparticle of the top layer is supported by at least three nanoparticles, homogenously ordered in a triangulation. The arrangement of nanoparticles is a random triangulation where the centers of the nanoparticles form the triangulation vertices. Indeed, the experimental evidence shows that silica nanoparticles organize themselves in a triangular configuration (Supporting information Fig. S1). Therefore, altering the size of the first layer's nanoparticles will affect the distance between the nanoparticles of the top layer as well as their organization (triangular or square forms). Thus, changing the size of nanoparticles, the inter-particle spacing (i.e, distance) and the organization of nanoparticles (i.e, periodicity) are important features to determine whether water penetrates or not into the surface texture. This model design enables an efficient control of the distance between adjacent nanoparticles and thus the surface coverage density. As a consequence, the roughness will be adjusted in order to alter the water contact angle. Wang et al. have made a similar statements about a design of a sophisticated Mushroomed-like textured surface [24]. The authors tuned the size of Mushroomed-like pillars controlling thus the breakthrough pressure at which the droplet penetrates or not into the texture.

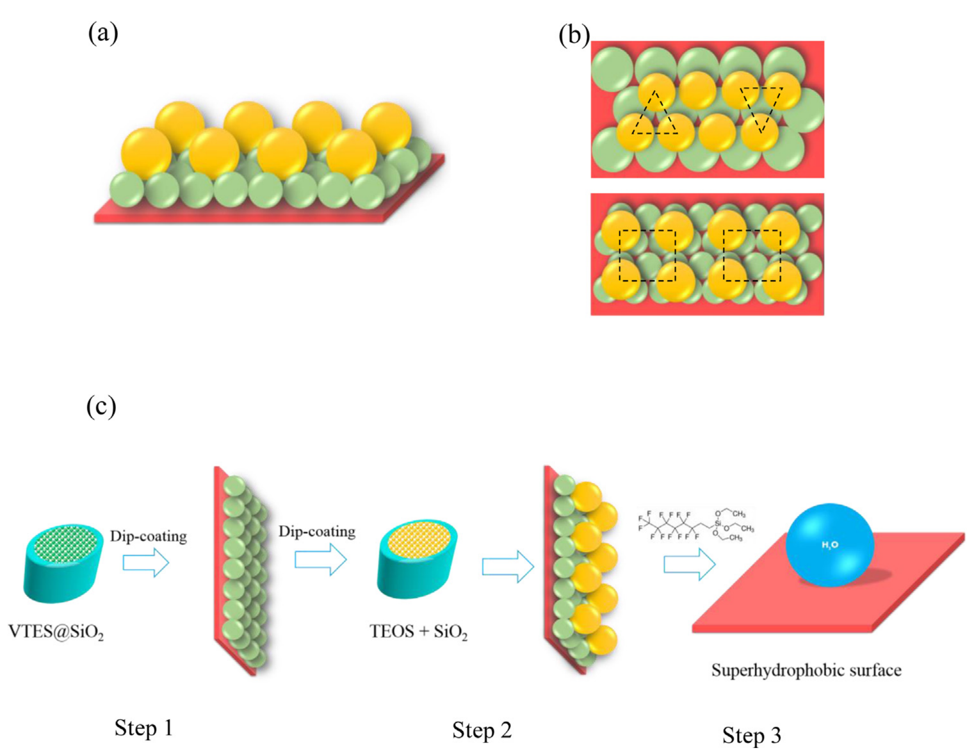


**Fig. 1.** Schematic representation of the coating (a) and the expected organization of nanoparticles (c) as function as the nanoparticles size of the first layer. (b) Schematic representation of the preparation procedure of the film with the formation of the first layer (Step 1), the deposition of the silica nanoparticles which the size is fixed at 100 nm (Step 2), and then their functionalization with hydrophobic molecule (step 3).