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# Superhydrophobic fluorine-free hierarchical coatings produced by vacuum based method



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## ABSTRACT

In this study it is presented fully vacuum-based, substrate independent method for fabrication of fluorine-free superhydrophobic surfaces based on combination of gas aggregation sources of nanoparticles and plasma polymerization. This method involves deposition of films of nanoparticles that are subsequently overcoated by plasma polymerized n-hexane. Two different kinds of nanoparticles that differ significantly in their sizes were used: small Cu nanoparticles (mean diameter 18 nm) and big plasma polymerized C:H nanoparticles (diameter 110 nm). It is demonstrated that superhydrophobic and slippery character may be achieved when surfaces with dual-scale roughness were prepared combining bigger C:H nanoparticles with smaller Cu nanoparticles.

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## 1. Introduction

Fabrication of surfaces with controllable roughness is the key step for production of biomimetic superhydrophobic surfaces inspired by the self-cleaning and anti-fouling properties observed in nature [1–3].

Based on numerous studies it is well established that the roughened hydrophobic surfaces have a larger area of contact between the surface and water droplet which enhances their hydrophobic character (homogeneous wetting regime [4]). In addition, certain level of roughness of a hydrophobic surface may result in trapping air beneath the water causing an increase of the contact angle (heterogeneous wetting regime [5]). The heterogeneous wetting is furthermore characterized by lower contact angle hysteresis that makes it more favorable for technological applications. However, heterogeneous wetting is in many cases not stable and may switch spontaneously or by external disturbance to homogeneous wetting regime that has often lower free energy and thus is thermodynamically more favorable [6].

One possible strategy for production of surfaces with stable heterogeneous wetting is based on fabrication of surfaces with hierarchical structures providing multi-scale surface roughness [7]. In this case the multi-scale surface protrusions form a high potential barrier between homogeneous and heterogeneous wetting regimes or even make homogeneous wetting physically

unrealizable [8]. As consequence various methods for production of surfaces with multi-scale roughness were developed. They are based for instance on chemical synthesis, imprinting, templating, e-beam or lithographic methods, layer-by-layer deposition, plasma etching etc. (e.g. recent reviews [9,10]). More recently also aerosol-assisted atmospheric plasma deposition was employed for surfaces with multi-scale roughness [11]. Although it was demonstrated that surfaces produced in these ways are superhydrophobic and slippery, the use of above-mentioned techniques is often hampered by certain limitations (e.g. use of potentially harmful solvents, time consumption, high costs and complexity or limited applicability to wider range of substrate materials). Moreover, majority of studies were focused on the fabrication of fluorocarbon coatings, since they possess the lowest surface energy. However, the use of fluorocarbons is somehow problematic, i.e. because of their possible health effects [12].

In this study it is introduced an alternative, fully vacuum based strategy of production of fluorine-free coatings that have dual-scale roughness and superhydrophobic character. Proposed strategy is based on the combination of two independent gas aggregation sources of nanoparticles and plasma enhanced chemical vapor deposition of hydrocarbon plasma polymer.

## 2. Experimental details

Set-up employed for samples preparation consisted of deposition chamber pumped by diffusion and rotary pumps, two gas

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aggregation sources (GAS) of nanoparticles and a source of plasma polymer. Si polished wafers, polypropylene foil and Si wafers coated with gold layer were used as substrate materials in this study.

Small copper nanoparticles (NPs) –  $18 \pm 6$  nm in diameter – were prepared by GAS based on a DC magnetron sputtering from a Cu target (51 mm in diameter) in Ar atmosphere. The current was set to 200 mA and the pressure of Ar in the aggregation chamber was 33 Pa. Deposition time of Cu NPs was 40 s. Similar GAS system was used also in case of plasma polymerized C:H NPs. The plasma polymerized particles were produced using a gas mixture of argon and hexane 7:1 at pressure inside the aggregation chamber 160 Pa. The radio frequency (RF) power applied to planar magnetron (51 mm in diameter) equipped with a carbon target was 40 W and the deposition time of C:H NPs was 300 s. The mean size of produced C:H nanoparticles was 110 nm. More details regarding the production of Cu and C:H NPs are given in [13,14].

Hydrocarbon plasma polymer film, which was used as a hydrophobic over-coating, was prepared by plasma polymerization in a mixture of Ar/n-hexane (7:1) at pressure 2 Pa. The RF power 80 W was delivered to the planar electrode 80 mm in diameter.

Morphology of deposited coatings was studied by means of scanning electron microscopy (SEM) (Tescan Lyra) and atomic force microscopy (AFM) (Quesant Q-Scope 350). Chemical composition of the coatings was investigated by X-ray photoelectron spectrometer (XPS) equipped with Al K $\alpha$  X-ray source (1486.6 eV, XR50, Specs). Wettability of produced coatings was measured by sessile water droplet method using a goniometer of custom construction.

### 3. Results

Four sets of coatings were produced in this study: 40 nm thick smooth C:H films, Cu nanoparticles overcoated by 7 nm thick C:H films, C:H nanoparticles overcoated by 50 nm thick C:H films and, finally, hierarchical coatings that are composed of layer of C:H nanoparticles, 50 nm thick layer of C:H, layer of Cu nanoparticles and top 7 nm thick layer of C:H. The schematic representation of

all prepared coatings is together with their SEM images presented in Fig. 1. The thickness of C:H layer was close to the one half of the mean diameter of the underlying nanoparticles in order to fix them on a surface.

All deposited samples were characterized by XPS. It has been found that surface elemental composition is equal for all samples independently of the presence of base layer of NPs. Only detectable peaks in XPS spectra were carbon (atomic concentration  $95 \pm 1\%$ ) and oxygen (atomic concentration  $5 \pm 1\%$ ). The presence of oxygen may be most likely attributed to the surface oxidation that occurred during the transfer of the samples from the deposition chamber to XPS.

The second studied parameter was surface roughness. As it is depicted in Fig. 2, the size of the nanoparticles that were used as the base layer has strong impact on the morphology of the samples and on their roughness. The coatings without any nanoparticles were smooth and characterized by root-mean-square (RMS) roughness below 1 nm. In contrast, coatings with Cu nanoparticle base layer had the RMS roughness  $4 \pm 1$  nm and films, for which big C:H nanoparticles were used, reached the value of RMS roughness  $88 \pm 9$  nm. The enhancement of surface roughness can be explained by the increase of the size of nanoparticles used as the base film [15,16]. In addition, AFM measurements revealed that coatings, for whose production were combined C:H and Cu nanoparticles, had surface roughness similar to the films prepared using solely C:H nanoparticles as the base layer ( $87 \pm 10$  nm).

Finally, the wettability of produced coatings was tested. Images of water droplets on all four kinds of samples deposited onto Si wafers are presented in Fig. 3. As can be seen the presence of Cu and C:H nanoparticles in the base layer led to substantial enhancement of the water contact angle by  $24^\circ$  and  $58^\circ$  as compared to smooth C:H film. This is consistent with increased surface roughness observed for Cu and C:H nanoparticles containing coatings. Nevertheless, the value of water contact angle did not overcome  $150^\circ$  even in the case of samples with the highest roughness and the samples retained rather high water contact angle hysteresis.

This situation markedly changed when small Cu and big C:H nanoparticles were combined and the surface had dual-scale

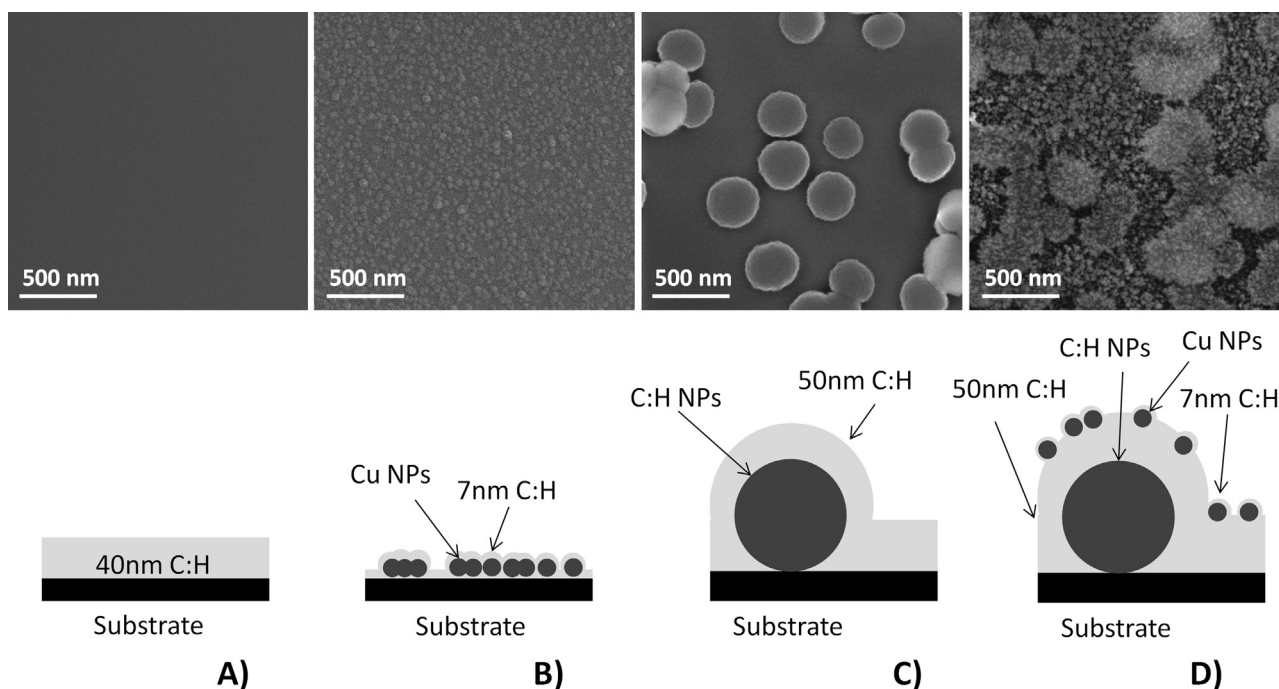


Fig. 1. SEM images and schematic representation of prepared samples.

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