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Textured superhydrophobic films on copper prepared using solvent-free methods exhibiting antifouling properties

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ABSTRACT

Development of superhydrophobic materials is in constant evolution due to their multiple applications. Recent investigations have shown that a stable and reliable superhydrophobic performance requires the use of hierarchical structures. In this work, we have engineered superhydrophobic copper surfaces using an innovative solution-free procedure to fabricate hierarchical structures. First, sequential cycles of O_2- and Ar-plasma etching were performed on the copper substrate to generate microtexture. Secondly, a fluoropolymer was deposited on top of the metal via initiated chemical vapor deposition (iCVD). The organic layer conformally coated the copper substrate maintaining the previously etched geometry. Moreover, the polymer displayed a very characteristic and unique structure with small protuberances arising out from the film in a nanoworm-like morphology. These nanofeatures together with the microroughness, induced by plasma etching, resulted in a hierarchical structure that confers superhydrophobic properties to copper. Water contact angle (WCA) as high as 168° and WCA hysteresis of 2° were measured for the treated samples. The superhydrophobic iCVD polymer was tested as an antifouling coating. Samples were exposed to *Pseudomonas fluorescens* for 24 h and the attachment of the microorganisms was reduced by 57% compared to uncoated copper.

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1. Introduction

The use of superhydrophobic materials has drawn special interest in many different applications, including self-cleaning, antifouling, microfluidics or energy conversion [1–6]. Superhydrophobic surfaces are characterized for having water contact angles (WCA) >150°, which can only be obtained by a combination of a low surface energy material and a textured surface. There are two different theories that give an explanation to this effect. Shortly, in the Wenzel or petal effect, the water drop is in full contact with the rough surface, while in the Cassie-Baxter or fakir state, there is air trapped in between the drop and the surface [7,8]. However, the Cassie-Baxter state is preferred in those applications requiring low adhesion between the liquid and the surface, that is, low CA hysteresis and roll-off angles. The achievement of this slippery state requires the design of a hierarchical structure, in which two different levels of roughness, micro- and nano-, are present. The micro- and nanostructures facilitate the trapping of air in the pockets minimizing the contact of water with the surface. In this sense, several studies have investigated the role of both texturing the surface and superhydrophobicity to reduce biofouling in materials [9–12]. Fouling is the attachment of microorganism in surfaces exposed to aqueous environments. Posterior growth and aggregation of bacteria and cells induce the development of biofilms. This fouling phenomenon causes the deterioration of the material and hence, a loss or failure in its performance.

Biofilm formation has been a serious problem in water treatment processes [13], fabrication of medical devices [14] or marine applications [15]. Furthermore, the growth of biofilms and proliferation of pathogens in water systems is considered as a potential health risk. For instance, *Salmonella, Escherichia coli* or *Pseudomonas* are pathogen agents that can be found in potable water causing waterborne diseases [16]. Copper is a widely employed metal in pipelines for water transport and thus, there has been several investigations studying the formation of biofilms on the metal [17,18]. Development of superhydrophobic coating on copper surfaces can be used as a valid strategy to diminish the attachment of microorganisms and prevent the formation of biofilms. In this work, we have designed a hierarchical coating on copper with low adhesion and superhydrophobic properties via two solution-free procedures. First, roughening the copper substrate by plasma etching, and then, depositing a low surface energy polymer by initiated chemical vapor deposition (iCVD). iCVD is a gentle and versatile polymerization method that allows surface functionalization

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preserving the delicate pendant groups of the monomers [19–21]. Changes in the topography of the substrate after the different processes were monitored by microscopy. The wettability of the surface was tested using WCA measurements. Finally, the antifouling properties of the coating were studied using *Pseudomonas fluorescens* as the model organism.

2. Experimental details

2.1. Chemicals and reagents

All chemical were used as purchased without further purification. Copper coupons (30 × 30 × 0.5 mm, 99.95%, Materials World) were used as substrate for the surface modification. 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA 97%, Sigma-Aldrich), ethylene glycol diacrylate (EGDA, PolySciences), tert-butyl peroxide (TBPO 98%, Luperox® DI, Sigma-Aldrich) were used for the iCVD polymerization. The antifouling experiments were conducted using *Pseudomonas fluorescens* (ATCC 13525, CECT), Trypticase Soy Broth (Merck), M9 Minimal Medium (Difco), phosphate buffered saline (PBS) crystal violet (CV) solution (Panreac) and acetic acid (>99%, Panreac)

2.2. Plasma etching

Copper samples were cleaned sequentially with acetone and isopropanol 5 min each in ultrasounds. Next, copper was treated with hydrochloric acid 0.1 M solution for 5 min in order to remove surface oxide. Clean copper samples were put into a custom-built tubular coil plasma reactor to conduct the plasma etching. A single copper sample is introduced in each experiment always in the same position of the reactor. Process consisted of two consecutives cycles with 2 different steps. Firstly, samples were treated with oxygen plasma at a working pressure of 14 Pa and power of 150 W for 4 min. Secondly, the surface was treated with argon plasma at a working pressure of 38 Pa and power of 40 W for 2 min. Next the second plasma cycle with the same conditions was applied. Samples were let to cool down at the reactor under argon atmosphere to avoid additional further oxidation.

2.3. iCVD polymerization

iCVD polymerizations were conducted in a custom-build cylindrical reactor (24 cm diameter and 4–6 cm adjustable height). On top of the reactor was placed a transparent quartz lid, which allows laser interferometry (633 nm He-Ne laser, Thorlabs) for in-situ monitoring of film thickness. The monomer PFDA and the cross-linker EGDA were heated in a metallic jar to 80 °C and 70 °C respectively and fed into the reactor chamber. The initiator, TBPO, was fed without heating. Flow rates were set to 0.15 sccm for PFDA, 0.10 sccm for EGDA and 2.0 sccm for TBPO using needle valves. In the reaction chamber a Ni/Cr (80/20, Goodfellow) filament was resistively heated at 220 °C, while stage was kept at 24 °C using a water recirculating system (Julabo). Distance between filament and stage was fixed at 25 mm. Working pressure was kept at 0.90 mbar, adjusting the aperture of the pump with a bellow valve.

2.4. Surface characterization

Thickness of iCVD films was estimated using laser interferometry on a silicon wafer. Films thickness ranged from 80 to 100 nm. Wettability of the superhydrophobic surfaces was evaluated by water contact angle measurements using a Drop Shape Analyser (DSA 100, Krüss). Advancing and receding contact angles were measured on 5 different points, using small drops of 5 μL. Atomic force microscopy (AFM) images were acquired with a XE-100 (PSIA Inc.) with lateral resolution of 0.15 nm and vertical of 0.05 nm, by non-contact mode. Images were analyzed by XEP and XEI software for data acquisition and image processing, respectively. SEM images were obtained using a Merlin FE-SEM (Zeiss) with acceleration voltage of 2 kV. Samples with non-conductive surfaces were coated with Pd/Au to avoid charging effects. Grazing Incidence X-ray diffraction (GIXRD) measurements were performed using a PANalytical X'Pert PRO MRD diffractometer with a PIXcel detector, a parabolic Göbel mirror at the incident beam and a parallel plate collimator at the diffracted beam, and with Cu Kα radiation (λ = 1.5406 Å at 45 kV and 40 mA). Data was collected at 0.3° min^{-1} with a step size of 0.04°.

2.5. Biological methods

In this study, iCVD polymer coatings were applied to copper coupons (10 × 10 × 1 mm), placed in a 12-well plate and submerge in biofilm-forming bacterium *Pseudomonas fluorescens* at 26 °C for 24 h.

2.5.1. Inoculum preparation

Pure cultures of gram negative *Pseudomonas fluorescens* were grown overnight in 50 mL Trypticase Soy Broth at 26 °C. Bacterial cells were harvested at the mid-exponential phase of growth by centrifugation at 10000 g in a SIGMA 3–16 K refrigerated centrifuge for 10 min, washed and resuspended in sterilized M9 Minimal Medium after centrifuging again. Bacterial dilution using M9 medium was performed to set the OD600 to 0.4, corresponding to 5×10^7 cells/mL.

2.5.2. Static cell adhesion assays

Square copper coupons (3 samples) were placed at the bottom of sterilized 12-well culture testplate (SPL Life Science) and 4 mL of the above bacterial suspension was added to each well. The system was incubated at 26 °C for 24 h without shacking. After incubation, samples were gently rinsed 3 times with 25 mL sterile PBS in order to remove any planktonic bacteria.

Bacterial attachment on coupon surfaces was quantified following a previously described crystal violet staining method [22] with few modifications. Briefly, coupons were allowed to dry for 1 h and placed in new wells. Each coupon was stained with 200 μL of 0.1% crystal violet (CV) solution for 10 min at room temperature and then rinsed five times with water to remove excess stain. Coupons were air dried for 1 h. After transferring to new wells, the dye incorporated into the adherent cells was solubilized with 1 mL of 30% acetic acid in water for 10 min. Absorbance of the dissolved solution was measured at 550 nm (Helios α Unicam spectrophotometer) using 30% acetic acid as the blank. The assay was also performed on no inoculated coupons (without bacteria) in order to serve as control.

3. Results and discussion

Surface modification of copper, involving plasma etching and iCVD polymerization, was conducted to yield a hierarchical structure. Experimental conditions for the plasma etching were optimized to texturize the metallic surface. The sequential use of oxygen and argon plasma was combined to control the degree of oxidation of copper and to enable the etching of the substrate. Clean copper coupons presented a flat surface with a roughness of 40 nm. By contrast, copper turned into a crease-shape morphology (Fig. 1a) and the roughness increased to 430 nm after the etching procedure as a consequence of the ion bombardment. Furthermore, Fig. 1b reveals the nanostructuration of the surface due to the copper oxidation. The copper oxide film presents a homogeneous grain size distribution of around 50 nm, similar to the values found by Souza et al. [23].

Next, the roughened copper was coated with the p(PFDA-*co*-EGDA) copolymer using iCVD to functionalize the surface with a low surface energy material. The polymeric layer was deposited preserving the modified topography of copper. The conformal nature of iCVD has been previously demonstrated by coating the contour of trenches, 3D objects and complex substrates with a uniform thickness and without

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