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Multifunctional surfaces from multi-step generation of silver thiolate

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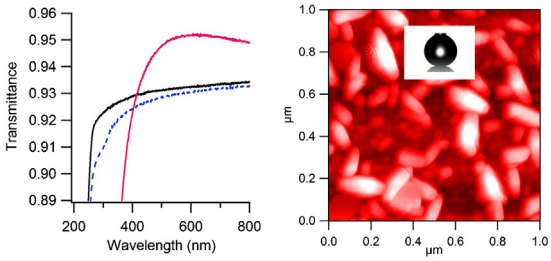
HIGHLIGHTS

- Silver thiolate layers result from successive immersions of a substrate in Ag nitrate and thiol solutions.
- The first and the following generations of silver thiolate come from different formation mechanisms.
- The consequence is that the 2nd generation of thiolate has much bigger grain size than that of the 1st one.
- These features permit to build superhydrophobic surfaces with sample transparency greater than silica.
- The making of multifunctional surfaces is exemplified using silver thiolates of two different natures.

GRAPHICAL ABSTRACT



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ABSTRACT

In this article, a novel methodology is studied for making multifunctional surfaces with multilayers of silver thiolate complexes. The method consists, first, in the catalytic generation of a silver thiolate film (first generation) from immersion of silver nanoparticles on a ZrO_2-coated substrate in a thiol solution. Then, successive steps of sample immersion in silver nitrate and in thiol solutions lead to silver thiolate layers of higher generations. The specificity of these latter layers is a much bigger grain size than the one in the layer of the first generation, owing to a new mechanism of formation. This property is used for building superhydrophobic and transparent coated substrates. Owing to sol–gel deposition of ultra-thin ZrO_2 layers, the anti-reflective effect of the silver perfluorodecanethiolate layers diminish the light reflection on the silica substrate. It is also shown that other functionalities can be added to the surface with the successive use of thiol solutions of different nature.

1. Introduction

Multifunctional surfaces are highly desirable for new technological applications. One of the most required properties is superhydrophobicity. Superhydrophobic surfaces are defined as surfaces for which the equilibrium contact angle of a drop of water is at least 150° and the contact angle hysteresis is less than 10° [1]. Drops of water can easily roll on such surfaces which are, then, self-cleaning. This property is very useful for extending the application range of multifunctional materials [2] and transparent glasses [3], for examples, to a natural environment. Superhydrophobic coating on a convex tube has also been demonstrated, allowing for the tube flotation on water surface, owing to water-repellent property [4]. After the works by Wenzel [5] and Cassie-Baxter [6], it is known that superhydrophobic surfaces are not only low surface energy but also

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are rough surfaces. So, transparency and superhydrophobicity are antagonistic properties, and a satisfactory compromise has to be found concerning the roughness scale for avoiding light diffusion. This problem has been overcome by many research groups [7-10].

Minimizing light reflection on a substrate with an antireflective coating is a mean for increasing the performance of optoelectronic devices or solar cells [11]. Recently, broadband antireflectivity has been obtained in combination with superhydrophobicity, owing to nanostructured graded-index coatings. In this way, sophisticated fabrication techniques, such as silver catalytic etching of silicon wafers [12], silica nanoparticle coating of surface glasses [13], nanolithography [14] or colloidal lithography [15] of silica surfaces have been developed.

A few years ago, methods for making bifunctional surfaces with superhydrophobic and plasmonic properties were reported by Li et al. [16] and Brenier [17]. In this latter work, silver nanoparticles were first obtained from the chemical method of oxide initiated silver nanoparticle generation on ZrO_2-coated Pyrex substrates. Then, the samples were immersed in a solution of perfluorodecanethiol in heptane. Since our very recent work [18], it is presently known that such a procedure leads to a partial catalytic transformation of the silver nanoparticles into silver perfluorodecanethiolate grains at room temperature. The transmittance of the sample clearly showed the presence of remaining silver nanoparticles after their generation time of 24 h owing to the plasmon band. Nevertheless, although the silver perfluorodecanethiolate grains on ZrO_2 are of low surface energy, their size was too small for preventing the invasion of water in the inter-grain space and the surface was not superhydrophobic. In order to substantially favor the grain growth, the ZrO_2 surface had to be covered with silane. In this latter case, the silver perfluorodecanethiolate grains could have a size large enough for a drop of water to remain on their summits and the surface was superhydrophobic.

In the present work, we propose an original method for making multifunctional surfaces capitalizing on catalytic silver thiolate formation [18] on one hand, and using a new mechanism of thiolate formation, on the other hand. Our strategy consists in performing successive steps of immersion in the silver nitrate and in the thiol solutions of ZrO_2-coated substrates. In Section 3.1, a fundamental study is reported and the making of the successive substrate coatings is characterized step by step by optical, atomic force microscopy and X-ray diffraction measurements. The decanethiol solution is chosen because the silver decanethiolate complex can easily be identified by X-ray diffraction [19]. This study reveals a new mechanism of an unexpected and spectacular growth of silver thiolate grains. In Section 3.2, this important result is used for making superhydrophobic surfaces. It is shown how the generation of a very low amount of silver nanoparticles on "ultra-thin" ZrO_2 layers on silica substrates and a multi-step thiolate generation can lead to making a sample with a superhydrophobic surface and high transparency, owing to an antireflective effect. In Section 3.3, the versatility of our method is exemplified using two different thiols (decanethiol and perfluorodecanethiol) as a new way to make multifunctional surfaces.

Our method aims to extend the field of metallosupramolecular systems [20,21] with potential applications in material science [22], microfluidics [23], lighting technologies or sensors [24].

2. Experimental

In our experiments, silica and Pyrex substrates of dimensions 7.5 cm × 2.5 cm × 0.2 cm were used. These substrates were coated on both sides with a ZrO_2 layer by sol–gel. The sol was obtained [25] by mixing an equimolar quantity of zirconium n-propoxide with acetylacetone as a stabilizer. Some sample series were coated with a "thick" and other sample series with an "ultra-thin" ZrO_2 layer, owing to different sol dilutions and solvents. For the thick layer, 3 cm^3 of Zr n-propoxide 70% solution in propanol was used. Finally, this sol was diluted with 16 cm^3 of isopropanol. For the ultra-thin layer, 1.5 cm^3 of Zr n-propoxide 70% solution in propanol was diluted with 16 cm^3 of isopropanol. Then, 4 cm^3 of this sol was again diluted with 8 cm^3 of isopropanol and 8 cm^3 of heptane.

For both types of coatings, the substrates were dipped in the sol and withdrawn at the speed of 8 cm/min. After drying at 100 °C in air for 10 min, the coated substrates were annealed in a furnace under oxygen atmosphere for 30 min.

For silver deposition on the ZrO_2-coated substrates, we made use of the chemical method of oxide initiated silver nanoparticle generation [26]. Briefly, both the substrate and a bottle containing an ethanolic solution of silver nitrate (5 mM) were, first, separately placed in an electric oven preheated at the temperature of 32 °C for 1 h, in order to stabilize their temperature. Second, the substrate was soaked in the bottle and the whole was placed in the oven. After a chosen silver generation time (1 or 2 h), the substrates were rinsed, without drying, owing to successive transfers into 4 bottles containing pure ethanol for the first one, mixing ethanol–heptane (2/3–1/3 volumic) for the second one, mixing ethanol–heptane (1/3–2/3 volumic) for the third one and pure heptane for the fourth one.

For treatment of the silver nanoparticles, the sample was immersed in a solution of 1H,1H,2H,2H-perfluorodecanethiol (2 mM) or 1-decanethiol (2 mM) in heptane for one night. During the sample immersion, no stirring of the solution was performed.

The transmittance and the reflectance of the samples were measured in a Lambda900 spectrophotometer from Perkin-Elmer. The incident angle was of 4°. The Ag nanoparticle surfaces were imaged by an atomic force microscope (AFM). An Asylum instrument was used in tapping mode with a driven frequency of about 100 kHz and a scan rate of 1 Hz. The wetting properties of the different surfaces were measured using the sessile drop method. The advancing θ_a and receding θ_r contact angles of a drop of distilled water (10 μl), deposited on the surface with a syringe of 0.5 mm diameter, were optically measured with an accuracy of ±2°. X-ray diffraction was performed using a Rigaku diffractometer equipped with a rotating anode operating at 9 kW. The beam was monochromatized with a two reflection Ge(220) × 2 crystal which selects the Cu-Kα1 radiation at the wavelength of 0.15406 nm. The measurements were performed in the θ–2θ geometry.

3. Results and discussion

3.1. Silver decanethiolate formation

The morphological and the optical studies of the silver decanethiolate formation are presented in Figs. 1 and 2, respectively. After the substrate immersion in the silver nitrate solution for 1 h, the amount of silver generated on the surface of the thick ZrO_2 layer is so weak that the AFM image (Fig. 1A) does not clearly show any silver nanoparticle. Nevertheless, the surface roughness (ratio r of the true to the projected area) is $r = 1.023$ which is significantly higher than the roughness of a silane-coated ZrO_2 surface [17] ($r = 1.001$).

In the same way, neither the transmittance (spectrum 1 in Fig. 2A) nor the absorptance (spectrum 1 in Fig. 2C) of the sample clearly show the plasmon band of the silver nanoparticles expected around $\lambda = 440$ nm. Nevertheless, the transmittance is slightly lower than that of the ZrO_2-coated silica substrate (spectrum s) exhibiting two extrema located at 254 and 410 nm coming from the Fabry–Perot resonances the ZrO_2 layers.