One-Step Method to Fabricate Transparent Super-Repellent Coatings Using Plasma Polymerization

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Abstract: We report a one-step and versatile approach to create transparent, self-cleaning, super-repellent surfaces using an environmentally-friendly process, namely plasma polymerisation. The resulting coatings are characterized by ultra-high liquid contact angles (>170°) and sliding angles equal to zero. Furthermore, these polymeric thin films are transparent, can be deposited indifferently on a multitude of substrates and were successfully tested for self-cleaning purposes.

Keywords: Plasma polymerisation, super-repellent, transparent, self-cleaning.

1. Introduction

Superhydrophobic surfaces can be used for different purposes, including extreme water-repellency, self-cleaning, anti-icing and cell repellency. The range of applications and the interest in these surfaces have enormously increased during the last years. Particularly, superhydrophobic surfaces with good optical transparency have attracted much attention and research due to the potential application in self-cleaning windows, optical devices, and solar cell modules [1-3]. However, most transparent superhydrophobic surfaces suffer from a lack of mechanical robustness, thermal stability and ultraviolet radiation resistance. Besides, coatings with optimal water-repellency property are usually less transparent than the bare substrate because surface roughness is a crucial parameter contributing to superhydrophobic performance but is detrimental for the coating transparency. Therefore, the fabrication of superhydrophobic water-repellent surfaces with high transmittance in addition to good mechanical robustness remains a major challenge.

To obtain a superhydrophobic behaviour, a surface requires both micro- and nano-scale roughness and a low surface energy. During the last 20 years many methods have been published to produce superhydrophobic surfaces [4-9]. Current superhydrophobic processes involve both multi-step procedures and harsh conditions, leading to expensive processes, which are in addition only applicable to relatively small samples, flat surfaces and/or limited nature of materials.

In this work, we described a one-step, universal and environmentally-friendly method to prepare highly transparent, self-cleaning (both in air and in oil) and durable coatings on various types of substrates (for example, flexible or rigid, flat or textured, and transparent or opaque). The super-repellent coating was obtained by plasma polymerisation of perfluorooctyl acrylate (PFAC). A spatial control of plasma polymerization enabled the deposition of a plasma coating with desirable morphological properties depending on the sample position from the glow discharge and from the plasma parameters (deposition time and RF power).

2. Experimental procedure

Perfluorooctyl acrylate was introduced in a stoppered glass gas delivery tube and degassed by performing three freeze−pump−thaw cycles. PFAC thin films were deposited on substrates by using a home-built radio frequency plasma reactor as described elsewhere [10]. The substrates were placed onto a glass support in a “discharge plasma” configuration. The copper coils were connected to an L–C matching network and a radio frequency generator providing an output frequency of 13.56 MHz. Plasma polymerization of PFAC was performed at a constant pressure of 0.3 mbar and molar flow rate of 0.9 $\mu mol.s^{-1}$. When the generator was switched off, the PFAC feed was valved off and the reactor chamber was pumped down to base pressure prior to venting up to atmosphere.

The (non)-wettability behavior of the surface has been evaluated by contact angle measurements. Surface chemistry has also been characterized by X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (ATR-FTIR). Atomic force microscopy (AFM) enabled the imaging of the morphology of the resulting coating. The total (i.e. specular and diffuse) transmittance were measured in the wavelength range of 390 to 800 nm by using a UV−Vis−NIR spectrophotometer. In addition, the durability and robustness of the functional polymer thin films was investigated.

3. Results and discussion

2.1. Spatial control of plasma polymerization

Surface morphology with a dual-scale roughness has been proved to be essential to create superyhydrophobictiy. One of the main advantages of plasma polymerization is that one is able to control both the chemistry and the texturing of the polymer coating surface. During the deposition, a spatial control of plasma polymerization enabled the deposition of plasma coatings with various morphologies depending on the sample position from the glow discharge: in the pre-discharge zone, discharge zone and post-discharge zone (Fig. 1).

Indeed, the AFM images (Fig.1) show coatings including particles having various sizes depending on the position of the substrate in the plasma reactor. Particularly, the coating obtained in the discharge zone clearly exhibits a hierarchical structure with both a nano-scale roughness (globular morphology) and a micro-scale roughness (due to particles assemblies). In contrast, the PFAC plasma coatings deposited in the pre-discharge and the post-discharge zones contain poorly-defined, irregular, amorphous features. From these results, we chose to work only in the discharge zone to design transparent super-repellent coatings.

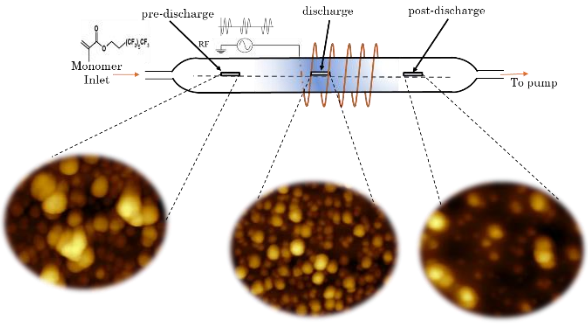

Fig.1. Schematic illustration of the low-pressure plasma reactor used for this study. The different studied positions of the sample are indicated (pre-discharge, discharge and post-discharge) and the AFM images of coating surfaces obtained at each discharge position are illustrated.

Infrared spectroscopy showed that the characteristic C=C bonds absorbance at 1638 and 1412 cm^{-1} associated with the PFAC monomer disappeared during plasma polymerization (Fig. 2 (left)), while C-F (1240-1145 cm^{-1}), C=O ester (1735 cm^{-1}), and C-H (2940 cm^{-1}) groups were still evident.
XPS analysis of the PFAC plasma polymer surfaces gave carbon, oxygen, and fluorine elemental that were very similar to the stoichiometry of the PFAC monomer. However, the high-resolution C(1s) envelopes could be fitted to eight different types of carbon environment (Fig. 2 (right)).

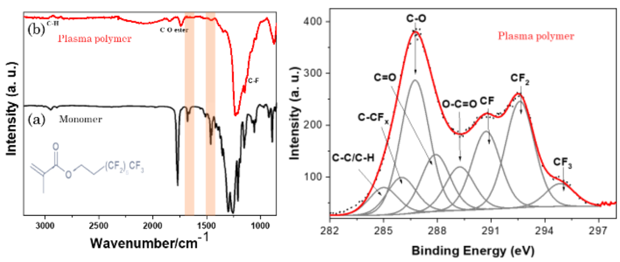

Fig. 2. Infrared spectra of 1H,1H,2H,2H-perfluorooctyl acrylate (left): (a) monomer; (b) PFAC plasma coating. XPS high-resolution spectra of C1s of PFAC coating (right).

2.2. Plasma parameters control: transparency vs roughness

Surface roughness competes with transparency, thus structures must be precisely tuned to achieve both high transparency and superhydrophobic behavior. The roughness can be directly controlled by a careful choice of plasma polymerization process parameters, as they alter the size distribution of nanostructures. To find a good compromise between transparency and surface roughness, we studied transmittance and surface roughness of plasma coatings as a function of two plasma process parameters: RF power and deposition time. Fig. 3 shows the variation of transmittance as a function of RF power and deposition time. Two domains are observed. When RF power is less than or equal to 50 W, the transmittance strongly increases with the power and decreases with the deposition time. The deposited plasma coatings are superhydrophobic. However, when the RF power is higher than 50W, the transmittance does not considerably vary with the deposition time and the resulting plasma coatings are high transparent and hydrophobic.

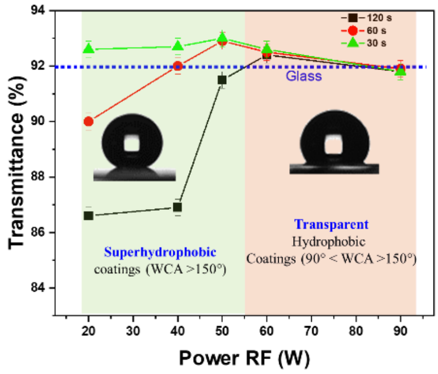

Fig. 3. Transmittance (λ = 600 nm) of PFAC coatings plasma as a function of power RF and deposition time. Inset: Digital photograph of water liquid droplet on the plasma coating.

We also determined the roughness of plasma coatings as a function of RF power and plasma treatment time. Fig. 4 shows that whatever the deposition time, the surface roughness decreases with the RF power. However, two distinguishable domains can be observed in the variation of roughness as a function of deposition time. When the power is less than or equal to 50 W, the roughness strongly varies and increases with time resulting in plasma coatings with a superhydrophobic behavior. Nevertheless, when the RF power is higher than 50W, the roughness slightly varies with the deposition time and the resulting plasma coatings are only hydrophobic.

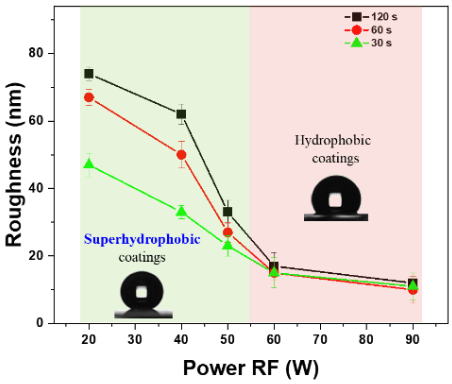

Fig. 4. Roughness of PFAC coatings plasma as a function of power RF and deposition time. Inset: Digital photograph of water liquid droplet on the plasma coating.

Fig. 5 shows the transmittance as a function of the surface roughness of the plasma coatings. The results clearly show that the surface roughness competes with the transmittance. As the surface roughness increases, the transmittance decreases. By coupling these results to surface wettability, three types of coatings can be distinguished: transparent hydrophobic coatings for a roughness values below 20 nm, superhydrophobic coatings for roughness values above 50 nm, and finally high transparent and superhydrophobic coatings for roughness values between 20 and 50 nm.

From these results, we can conclude that the plasma parameters that give a good compromise between transparency and surface roughness, thus having coatings with both excellent transparency and super hydrophobic behavior are: an average RF power of 40 to 50 W and a deposition time of 30 to 60 s.

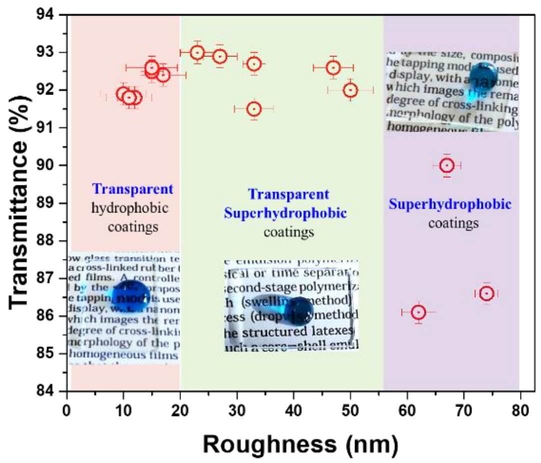

Fig. 5. Transmittance vs roughness of PFAC coatings plasma. Inset: Optical photos of methylene blue dyed water droplets on coated glass substrate.

2.3. *Wettability and self-cleaning behavior of PFAC coated glass*

A multi-scale roughness provides PFAC coatings with super-repellant properties. This behavior is assumed to originate from the two levels of roughness and the low surface energy of the plasma coatings. Moreover, the combination of these properties provides ultra-small local contact areas with the liquid. This is shown by the ultrahigh contact angles (> 150 °) obtained for the probe liquids tested. Besides, the PFAC coating exhibits extreme liquid repellency to many of these liquids (>35 mN.m^{-1}), with the near-zero sliding angle.

The super-repellant surfaces also featured a self-cleaning property. Fig. 6 shows the self-cleaning behavior of a PFAC super-repellant coating. When dust is positioned on the coating and water is dropped, the water droplets roll away from the coating carrying the dust away (Fig. 6a). After being washed with water, a clean coating is left, indicating a good self-cleaning property of the coating. Similarly, muddy water quickly rolls away from the coating (Fig. 6b), leaving a clean PFAC coated glass surface.

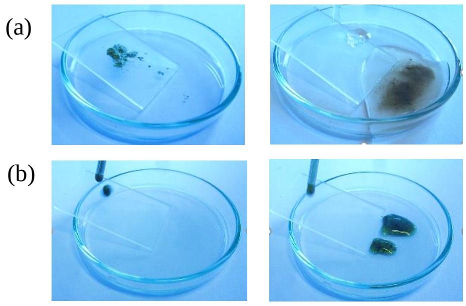

Fig. 6. (a) Self-cleaning processes for the PFAC coated glass surface. (b) Resistance to muddy water drops for the coated glass surface in antifouling tests.

2.4. Optical transmittance of PFAC coated glass

The super-repellant and self-cleaning coatings also exhibit high optical transmission. Fig. 7 shows the optical transmission as a function of wavelength, for uncoated glass and PFAC plasma coated glass. One can observe the antireflection property of the nanotextured glass surface. The average transmission over the 500 to 800 nm range increases from 91.5% for uncoated glass to 93.5% for PFAC coated glass. This increase in transmittance might be due to the presence of porous interconnected nanospheres that can confine incident, scattered and reflected light towards the glass surfaces [11,12].

2.5. Durability tests of PFAC plasma coating

The robustness and stability of super-repellent coatings on the substrates are critical to practical applications.

A continuous water drop test was used to study the robustness of the super-repellent PFAC coating. After 6L water dropping impact, the wettability of the super-repellent coating on glass substrates does not change.

The temperature stability of the coatings was also evaluated from -18 to 200°C. The super-repellent properties of coatings remained unchanged in the tested conditions. Moreover, it seemed that a UV irradiation time within 4h had almost no effect on wettability of the PFAC coating. In addition, when the PFAC coated glass surface was placed for 12 months in the lab, the sample still retained a large water contact angle and near-zero sliding angle.

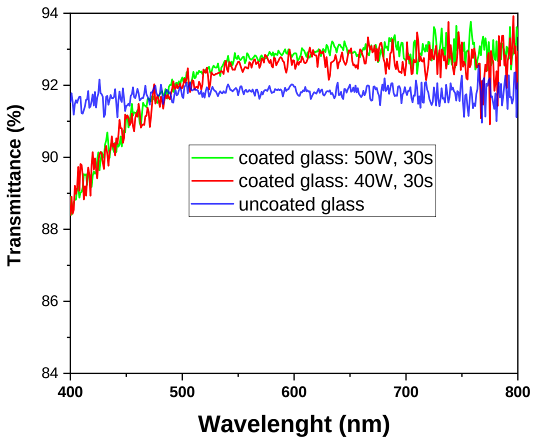

Fig. 7. Direct optical transmission of uncoated and coated glass as a function of wavelength.

2.6. PFAC coated on various substrates

Besides the glass substrate, other substrates can be coated with PFAC coating. No matter how rigid or flexible, rough or flat, hydrophobic or hydrophilic the substrates, a super-repellent coating can be obtained successfully. In this work, silicon wafer, aluminum, steel, cotton, wood, paper, PET, PMMA and PDMS were used as substrates. Those substrates were successfully coated with super-repellent PFAC coating.

4. Conclusion

A highly transparent self-cleaning super-repellent coating was developed via a one-step and versatile approach. A dual-scale roughness, super-repellent PFAC coating was obtained by plasma polymerization. The PFAC plasma coating demonstrates universal substrate-independent properties and could cover various kinds of substrates to realize super-repellent surface. The resulted coating also exhibits excellent optical transmittance and self-cleaning properties in air. Water dropping impact, temperature effect and UV exposition tests indicated that this transparent super-repellent coating exhibits excellent durability and stability. The transparent super-repellent coating could make an ideal material for applications in photovoltaic systems, optics, optoelectronics, liquid repellent coatings, and oil-water separation.

5. References

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