

# Preparation of Superhydrophobic Coatings on Zinc, Silicon, and Steel by a Solution-Immersion Technique

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**ABSTRACT** Zinc, silicon, and steel superhydrophobic surfaces were prepared by a simple solution-immersion technique. In the case of zinc, the method consists of dipping of the substrate in a prehydrolyzed methanol solution of 1*H*,1*H*,2*H*,2*H*-(perfluorooctyl)-trichlorosilane [CF<sub>3</sub>(CF<sub>2</sub>)<sub>5</sub>(CH<sub>2</sub>)<sub>2</sub>SiCl<sub>3</sub>, PFTS] for 24 h at 50 °C. Micron-sized spheres (1.7–2 μm in diameter) were formed on the zinc substrate at 50 °C, while a featureless coating was obtained when the solution-immersion process was conducted at room temperature. When the reaction was performed at room temperature, the formation of superhydrophobic coatings took several days (up to 5 days). In contrast, immersion of silicon or steel substrates in the PFTS/methanol solution led to the formation of hydrophobic interfaces even for a prolonged immersion period at 50 °C. The formation of superhydrophobic surfaces on silicon and steel surfaces was only possible if a zinc foil was added in the PFTS/methanol solution containing the silicon or steel substrate. X-ray photoelectron spectroscopy analysis was used to characterize the resulting surfaces and to underline a plausible reaction mechanism.

**KEYWORDS:** superhydrophobic coating • zinc • silicon • steel • solution immersion

## 1. INTRODUCTION

The fabrication and use of solid surfaces with superhydrophobic and/or superamphiphobic character were recently intensively studied (1). These surfaces display a water contact angle higher than 150° and often a low hysteresis. A water droplet deposited on these surfaces has a tendency to roll off upon tilting of the surface by few degrees. Superhydrophobic surfaces hold promise for potential applications such as self-cleaning interfaces (2, 3), for electrowetting-based applications (4–7), and anticorrosion layers (8, 9).

Surface superhydrophobicity is an interplay between the surface roughness and its chemical composition. Numerous methods have been developed to fabricate artificial superhydrophobic surfaces including lithographic patterning (10), electrodeposition (11), and others (12). Chemical deposition techniques are good alternatives because they do not require any particular equipment and allow easy process control (13–16). Different approaches have been described up to

now in the literature. A solution-immersion process for the fabrication of superhydrophobic steel, copper, and titanium surfaces was proposed by Zhang et al. (15). The technique consists of wet chemical etching and surface coating with a fluoroalkylsilane. The chemical etching induces surface roughening required to reach a superhydrophobic state after chemical functionalization with low-surface free-energy molecules. Surface modification of an etched metallic species with (tridecafluorooctyl)triethoxysilane was used by Qian and Shen to form superhydrophobic interfaces (14). Jiang et al. prepared superhydrophobic copper plates by immersion into a fatty acid solution (13). Our group and others have reported on the formation of superhydrophobic copper, zinc, and galvanized iron interfaces (8, 9). The surface modification is based on a simple solution-immersion process. (Perfluorooctyl)trichlorosilane (PFTS) molecules are hydrolyzed in a first step before reacting in an interfacial condensation/polymerization reaction with the catalytically oxidized metal interface (8). The modification process is, however, rather long. The formation of a dense film of microspheres with an average diameter of 1.5–3 μm was only observed after 3 days of immersion of copper in the prehydrolyzed PFTS solution (8). Galvanized iron showed a honeycomb-like architecture with flower-like submicroscopic structures, which increases the overall surface roughness and is partly responsible for the superhydrophobic character. In the case of zinc, however, the surface morphology of the resulting superhydrophobic inter-

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faces was badly defined with no specific surface structures (8, 9). The superhydrophobic film on the zinc substrate provided, nevertheless, an effective corrosion-resistant coating when immersed in chloride-containing solutions (9).

Here we have used a simple immersion solution technique to form superhydrophobic films on zinc, silicon, and steel substrates. The technique consists of immersion of the solid substrate in a prehydrolyzed solution of (perfluorooctyl)trichlorosilane for 24 h at 50 °C. It is important to highlight the importance of the presence of a zinc substrate in the reaction mixture to ensure the formation of a superhydrophobic coating on steel and silicon surfaces. In the absence of a zinc substrate in the immersion solution, hydrophobic coatings were obtained on steel and silicon substrates. A mechanistic approach is presented to take into account the observed results and to propose a general scheme for the preparation of superhydrophobic interfaces.

## 2. EXPERIMENTAL SECTION

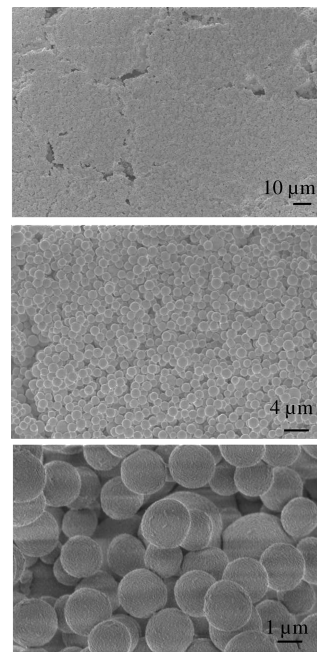
**2.1. Materials.** Zinc foil (99.9%, 0.25 mm thick), 1H,1H,2H,2H-perfluorooctyltrichlorosilane [ $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$ , PFTS], methanol, ethanol, and isopropyl alcohol were obtained from Aldrich and used without further purification. Single-side polished silicon (100) wafers were obtained from Siltronic (Archamps, France). The steel substrates were obtained from Arcelor (Paris, France) and have the following surface composition: Fe (8.1%), Cr (4.6%), C (33%), O (54.3%).

**2.2. Preparation of Superhydrophobic Interfaces.** The silicon substrates were ultrasonically washed with acetone and isopropyl alcohol, rinsed with Milli-Q water, and cleaned in a piranha solution (3:1 concentrated  $\text{H}_2\text{SO}_4/30\%$   $\text{H}_2\text{O}_2$ ) for 20 min at 80 °C followed by copious rinsing with water. The zinc (1 cm  $\times$  1 cm  $\times$  0.01 cm) and steel substrates were ultrasonically washed with 1:1 acetone/isopropyl alcohol (10 min, three times) and then with water. The interfaces were further cleaned using a UV-ozone cleaner [UVO cleaner, no. 42-220, Jelight Co. Inc. (Irvine, CA),  $P = 1.6 \text{ mW cm}^{-2}$ , distance from sample = 3 mm] for 1 h. The clean specimens were dried under a stream of nitrogen. A methanol solution of PFTS (4 mL of methanol and 35  $\mu\text{L}$  of PFTS) was hydrolyzed by the addition of a 3-fold molar excess of water (10 mL). The dried specimens were immersed in the hydrolyzed PFTS solution for 1–3 days at 50 °C, rinsed with ethanol and water, and finally heated at 130 °C in air for 1 h.

**2.3. Instrumentation. Contact-Angle Measurements.** Water contact angles were measured using deionized water. We used a remote computer-controlled goniometer system (Digidrop from GBX, Bourg de Peage, France) for measuring the contact angles. The accuracy is  $\pm 2^\circ$ . All measurements were made in an ambient atmosphere at room temperature.

**Scanning Electron Microscopy (SEM) Images.** SEM images were obtained using an electron microscope ULTRA 55 (Carl Zeiss Inc., Maple Grove, MN) equipped with a thermal field-emission emitter, three different detectors (a EsB detector with filter grid, a high-efficiency In-lens SE detector, and an Everhart-Thornley secondary electron detector), and an energy-dispersive X-ray (EDX) analysis device.

**X-ray Photoelectron Spectroscopy (XPS).** The chemical composition of the samples' surface was characterized by an X-ray photoelectron spectroscope (Microlab 350) using Al K $\alpha$  nonmonochromated radiation (1486.6 eV; 300 W) as the excitation source. The pressure during analysis was  $1.0 \times 10^{-9}$  mbar. The binding energy of the target elements (C 1s, Si 2p, F 1s, Zn 2p, and O 1s) was determined at a pass energy of 40 eV, with a resolution of 0.83 eV, using the binding energy of carbon



**FIGURE 1.** SEM images of a zinc substrate immersed in a prehydrolyzed solution of PFTS at 50 °C for 24 h.

(C 1s, 285 eV) as the reference. A linear or Shirley background subtraction was made to obtain the XPS signal intensity. The peaks were fitted using an asymmetric Gaussian/Lorentzian mixed function.

## 3. RESULTS AND DISCUSSION

**3.1. Formation of Superhydrophobic Zinc Surfaces.** Recently, we showed that hydrolyzed PFTS molecules can react in an interfacial condensation/polymerization reaction with the catalytically oxidized zinc to yield a superhydrophobic interface with a contact angle of  $151 \pm 2^\circ$  (9). While the superhydrophobic overcoating protected the underlying zinc substrate from corrosion during immersion in aqueous solutions with high chloride contents, the surface morphology of the superhydrophobic interface was not well-defined (absence of specific surface structures). Performing the surface reaction at 50 °C for 24 h instead of 5 days at room temperature (9) improved considerably the final surface morphology without losing the superhydrophobic character. The chemically modified zinc interface exhibits a maximum water contact angle value of  $151 \pm 2^\circ$  after 1 day of immersion in the hydrolyzed PFTS solution at 50 °C. Figure 1 shows SEM images of the superhydrophobic zinc interface. The resulting surface exhibits a structure composed of multilayers of uniformly dispersed particles with a particle size of 1.7–2.0  $\mu\text{m}$  and an average film thickness of  $\sim 10 \mu\text{m}$ . The success of the surface modification was, furthermore, confirmed by EDX analysis. The surface consists of Zn (13.50 wt %), O (6.78 wt %), Si (1.95 wt %), F (65.81 wt %), C (11.18 wt %), and Cl (0.78 wt %) elements. Compared to a superhydrophobic zinc surface prepared at room temperature for 5 days (9), a significant increase in the fluorine, silicon, and carbon concentrations is observed. The presence of chlorine in the EDX spectrum suggests that all of the Si–Cl bonds were not hydrolyzed during

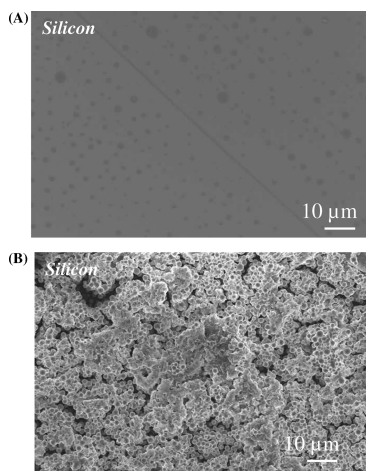


FIGURE 2. SEM images of a silicon substrate immersed in a prehydrolyzed solution of PFTS for 24 h at 50 °C in the absence (A) and in the presence of a zinc foil in the reaction solution (B).

the chemical process even at 50 °C. However, the chlorine concentration decreased from 1.96 wt % (room temperature, 5 days) (9) to 0.78 wt % (50 °C, 24 h).

**3.2. Formation of Superhydrophobic Silicon Surfaces.** The feasibility of this simple chemical strategy for the preparation of superhydrophobic silicon surfaces was investigated. Immersion of a clean Si/SiO<sub>2</sub> substrate into a hydrolyzed PFTS/methanol solution for 24 h at 50 °C resulted in a surface with a contact angle of  $107 \pm 2^\circ$ . The thickness of the final film was determined using profilometry measurements and was  $1.5 \pm 0.3 \mu\text{m}$ . This accounts for an average deposition rate  $v_{\text{deposition}} \approx 1.1 \text{ nm min}^{-1}$ . Performing the reaction for 2 and 5 days at 50 °C led to a slight increase of the contact angle to  $112 \pm 2^\circ$ . The thickness of the final film increased to  $2.8 \pm 0.3 \mu\text{m}$  after 2 days and had a final film thickness of  $4.3 \pm 0.3 \mu\text{m}$  after 5 days. This corresponds to average deposition rates of  $v_{\text{deposition}} \approx 1 \text{ nm min}^{-1}$  (2 days) and  $v_{\text{deposition}} \approx 0.6 \text{ nm min}^{-1}$  (5 days). However, in all cases, no superhydrophobic character was reached. The successful formation of a superhydrophobic coating is believed to be an interplay between the presence of fluorine, the most effective element for lowering the surface free energy because of its small atomic radius and largest electronegativity among all atoms, and the roughness of the interface (17). No distinct surface features, which could increase the surface roughness, can be observed on the modified silicon interface (Figure 2A). XPS was used to analyze the chemical composition and the nature of the chemical bonding on the modified silicon surface. From the XPS survey spectrum (Figure 3A), signals for F 1s (688 eV; 25.6 atom %), O 1s (532 eV; 19.2 atom %), C 1s (285 eV; 17.8 atom %), and Si 2s (151 eV) and Si 2p (99 eV) (with a total of 37.4 atom %) were observed, in accordance with the chemical composition of the PFTS molecule used in the solution-immersion process. The ratio of F/C is 1.44 close to the theoretical value of 1.62. The high-resolution XPS spectrum of Si 2p (Figure 3B) shows a main peak at 99 eV due to Si–Si bonds from the bulk and components at higher binding energies due to different oxidation states of silicon Si–O<sub>x</sub> bands. The C 1s high-resolution XPS spectrum indi-

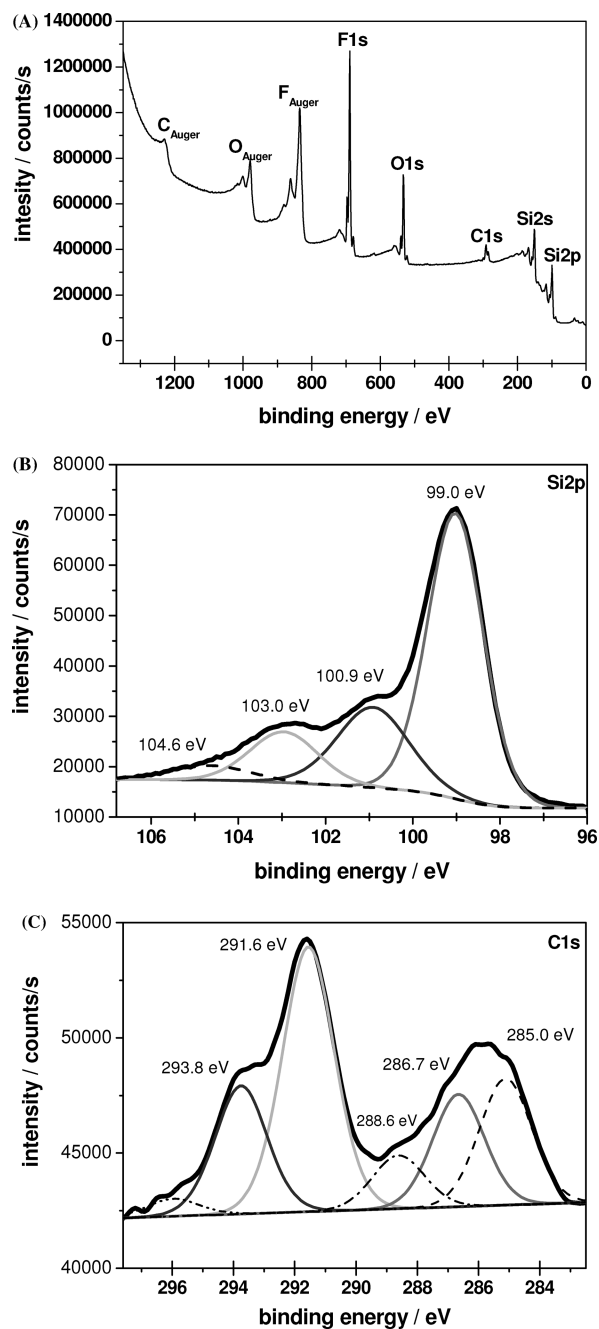
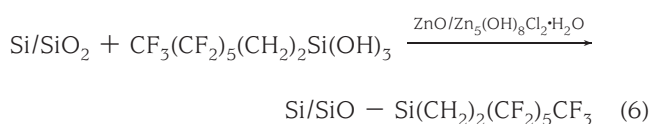
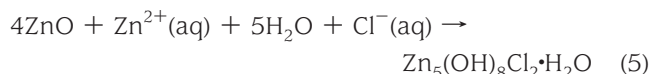
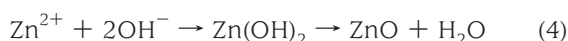
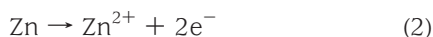
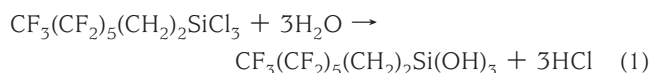


FIGURE 3. XPS survey (A) and high-resolution XPS spectra of Si 2p (B) and C 1s (C) of a silicon substrate immersed in a prehydrolyzed solution of PFTS for 24 h at 50 °C in the absence of a zinc foil in the reaction solution.

cates clearly the presence of  $-\text{CF}_3$  and  $-\text{CF}_2$  units at 293.8 and 291.6 eV, respectively, and a peak at 285.0 eV due to C–C bonds, in agreement with the chemical composition of the PFTS molecule (Figure 3C). The results are a clear indication that a fluorine-containing layer is formed on the silicon substrate. It was reported that, even though fluorine is present, a flat surface functionalized with closely packed  $-\text{CF}_3$  groups displays a water contact angle of  $119^\circ$  (18), close to the one observed in this work ( $112^\circ$ ). Additional bands at 288.6 and 286.7 eV corresponding to  $\text{O}=\text{C}-\text{OH}$  and C–O functions, respectively, are observed and were attributed to surface contamination.

Rather different results were obtained when the condensation/polymerization reaction of hydrolyzed PFTS molecules on a silicon substrate was performed in the presence of a zinc plate (with a total surface area of about 10 times smaller than that of silicon) at 50 °C for 24 h. A maximum water contact angle of  $151 \pm 2^\circ$  was recorded on the modified silicon interface as well as on the zinc foil present in the same solution. The presence of the zinc foil in the reaction solution changed significantly the morphology and roughness of the silicon interface (Figure 2B) and seems to be responsible for the measured contact angle. From the XPS survey spectrum (Figure 4A), signals for F 1s (688 V; 40.1 atom %), O 1s (532 eV; 18.0 atom %), C 1s (285 eV; 33.5 atom %), and strong XPS bands at 1023 and 1045 eV for Zn 2p (8.4 atom %) were detected. The high-resolution Zn 2p spectrum is seen in Figure 4B. The Zn 2p<sub>3/2</sub> XPS line for metallic zinc is located at a binding energy of 1021.8 eV. In the case of ZnO, chemical shifts are found at  $1021.8 \pm 0.7$  eV (19, 20). Deconvolution of the Zn 2p signals suggests, however, that probably two contributions may be assigned to ZnO and/or ZnCl<sub>2</sub> at 1022.5 eV. The C 1s high-resolution XPS spectrum (Figure 4C) can be deconvoluted into four components: The presence of -CF<sub>3</sub> and -CF<sub>2</sub> moieties are seen at 292.5 and 290.1 eV, respectively. The band at 285.0 eV indicates also the presence of C-C bonds. Because of surface contamination, an additional band at 286.7 eV corresponding to C-O is observed. The ratio of F/C is decreased from 1.44 (in the absence of zinc) to 1.19 (in the presence of zinc). From these observations, the following reaction mechanism is proposed.



In a first step, PFTS molecules are hydrolyzed in solution, inducing a decrease of the pH (reaction 1). Under acidic

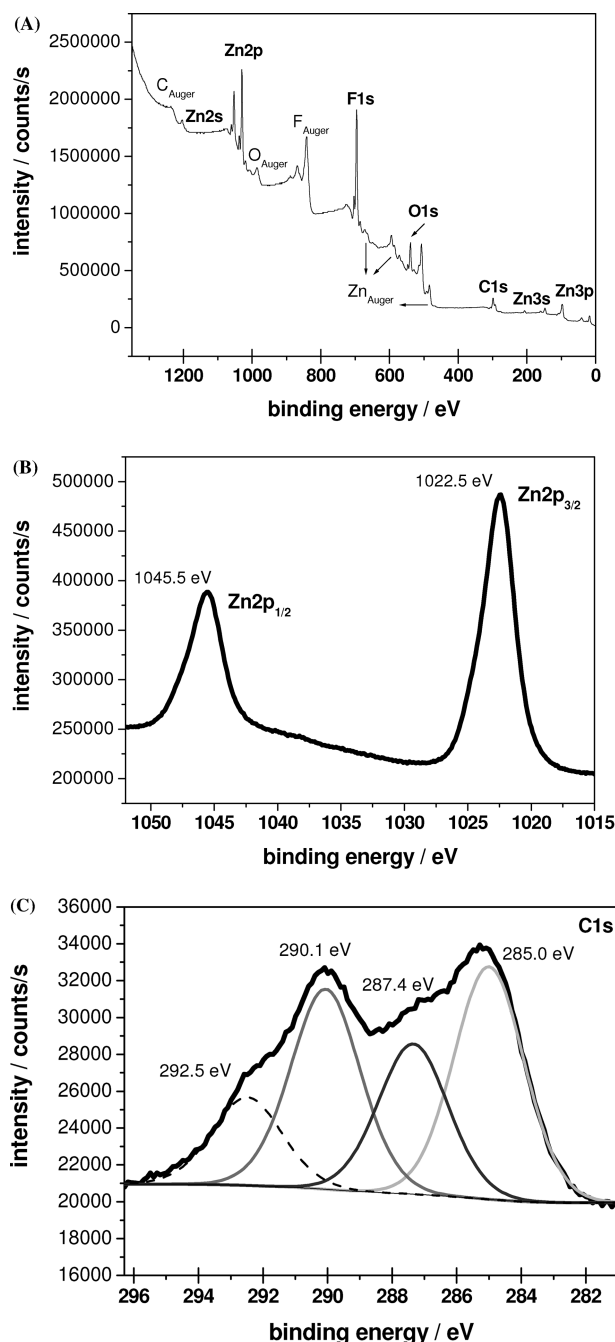


FIGURE 4. XPS survey (A) and high-resolution XPS spectra of Zn 2p (B) and C 1s (C) of a silicon substrate immersed in a prehydrolyzed solution of PFTS for 24 h at 50 °C in the presence of a zinc foil in the reaction solution.

conditions, zinc is catalytically oxidized, leading to the formation of zinc cations (reaction 2) and anodic dissolution of zinc. The reaction is balanced by the reduction of oxygen-producing hydroxyl ions (reaction 3). The hydroxyl anions react with  $\text{Zn}^{2+}$  to form zinc hydroxide (reaction 4). In a slightly acidic and alkaline solution, the thermodynamically more stable ZnO will be formed, which is insoluble and will precipitate onto the surface of the silicon wafer. To verify the proposed hypothesis, unmodified silicon interfaces were immersed in a methanol solution of hydrochloric acid at pH = 1 (the same pH as that in the case of the PFTS solution) for 24 h at 50 °C in the absence and presence of a zinc foil.

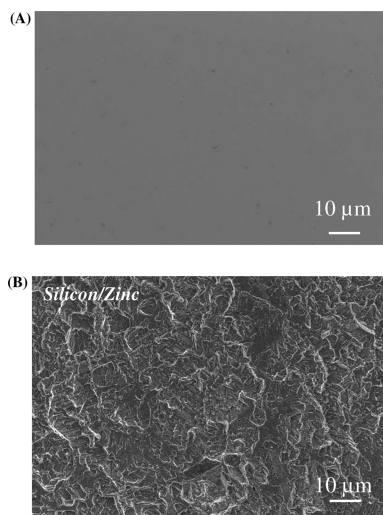


FIGURE 5. SEM images of a silicon substrate immersed in a methanol solution of hydrochloride acid at pH 1 for 24 h at 50 °C in the absence (A) and in the presence (B) of a zinc foil in the reaction solution.

Figure 5 shows the SEM images of the resulting interfaces. In the absence of zinc, the morphology of the initial silicon interface is not altered, while the presence of a zinc foil in the reaction mixture induces a significant change in the surface morphology, in agreement with the formation of zinc corrosion products such as simonkolleite and zinc oxide (21). This leads to an overall increase of the surface roughness and the formation of a superhydrophobic interface. Parallel to the deposition of zinc corrosion products onto silicon, it is believed that the hydroxyl groups of the silicon interface react in an interfacial condensation/polymerization reaction with the hydrolyzed PFTS molecules (reaction 6). The zinc corrosion products can thus be found directly on the interface as well embedded in the polymer structure. This is consistent with the XPS results, where the presence of  $Zn^{2+}$  was confirmed. Because the probing depth of XPS is about 10 nm, only the very top of the film is probed. In addition, the high-resolution XPS of Zn 2p indicates the presence of  $ZnX_2$  species. This can be attributed to the formation of either zinc chloride (reaction 7) or side products of anodic zinc dissolution, simonkolleite (reaction 5).

**3.3. Formation of Superhydrophobic Steel Surfaces.** The same strategy was investigated for the preparation of superhydrophobic steel surfaces. The presence of a zinc foil in the reaction mixture next to a steel substrate led to an increase of the contact angle from  $137 \pm 2^\circ$  (1 day at 50 °C) to  $151 \pm 2^\circ$  (2 days at 50 °C). This indicates the progressive formation of a superhydrophobic interface following the reaction mechanism outlined above for silicon. The surface of the zinc foil displayed in this case a final contact angle of  $144 \pm 2^\circ$ . As for the silicon substrate, the surface roughness was strongly increased when the zinc foil was present in the PFTS solution (Figure 6). However, no distinct surface features as in the case of superhydrophobic zinc were observed. A comparison of the XPS survey spectra of the modified steel in the absence (Figure 7) and in the presence of zinc (Figure 8A) shows clearly that, in the presence of zinc, a dense thick organic layer is formed on

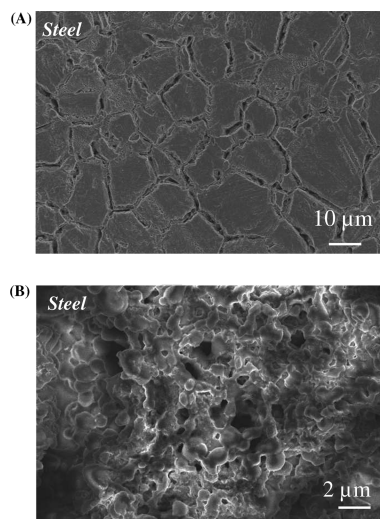


FIGURE 6. SEM images of a steel substrate immersed in a prehydrolyzed solution of PFTS for 2 days at 50 °C in the absence (A) and in the presence of a zinc foil in the reaction solution (B).

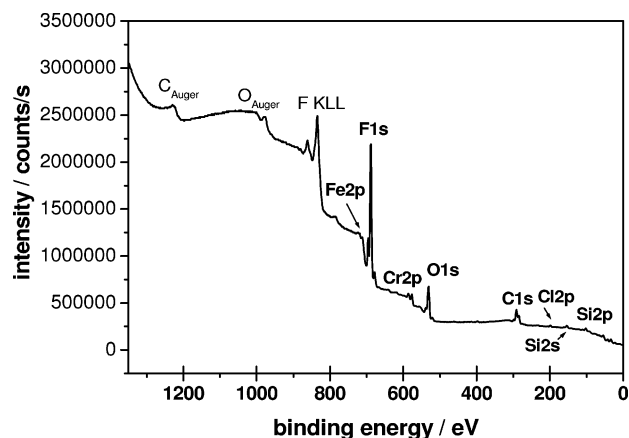
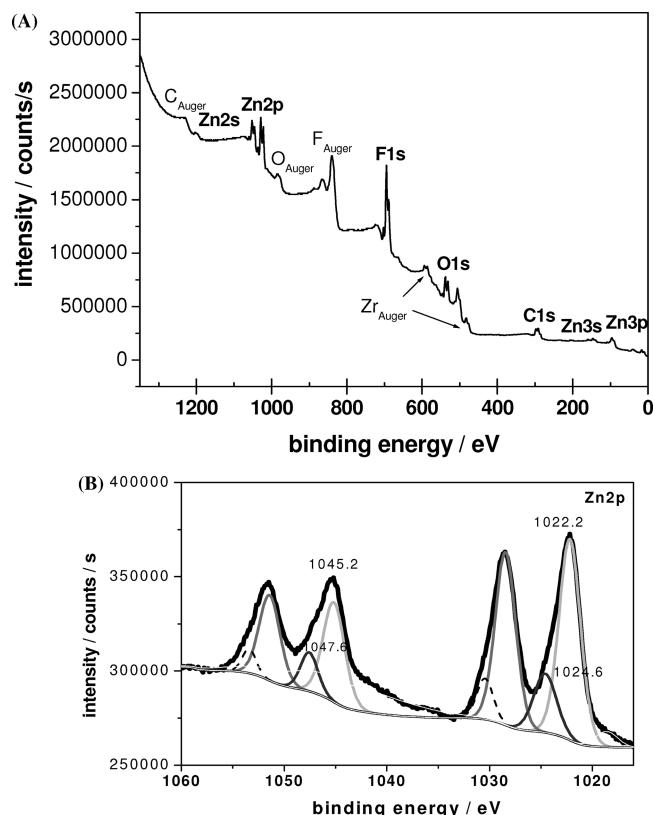


FIGURE 7. XPS survey spectrum of a steel substrate immersed in a prehydrolyzed solution of PFTS for 2 days at 50 °C in the absence of a zinc foil in the reaction solution.

steel, masking the underlying surface. From the XPS survey spectrum (Figure 8A), signals for F 1s (688 eV; 39.1 atom %), O 1s (532 eV; 22.8 atom %), and C 1s (285 eV; 33.4 atom %) and strong XPS bands at 1023 and 1045 eV for Zn 2p (4.7 atom %) were detected. While the atomic ratio of F/C was almost the same in both cases (1.10 and 1.17, comparable to the results on silicon), the presence of zinc is confirmed by XPS, showing bands due to Zn 2p, Zn 3s, and Zn 3p (Figure 8A). Deconvolution of the Zn 2p peak (Figure 8B) points toward the presence of ZnO and/or  $ZnCl_2$ , as observed in the case of silicon. However, the interpretation of the results for modified steel in the presence of zinc is complex. XPS shifts to higher binding energies and separation of the maximum peaks is observed for Zn 2p, which can be linked to the charging effect observed during XPS measurements.

#### 4. CONCLUSION

In summary, a general concept for the formation of superhydrophobic surfaces on metals and semiconductors was developed using a simple and effective solution-immersion process. It is based on the use of a PFTS where a zinc



**FIGURE 8.** XPS survey (A) and high-resolution XPS spectra of Zn 2p (B) of a steel substrate immersed in a prehydrolyzed solution of PFTS for 2 days at 50 °C in the presence of a zinc foil in the reaction solution.

foil is present in the reaction medium. A reaction mechanism accounting for the different species involved the chemical process is proposed. In parallel to the interfacial condensation/polymerization reaction, corrosion of the zinc foil and precipitation of zinc corrosion products onto the silicon and steel interfaces results in the formation of superhydrophobic interfaces. The superhydrophobic character was not reached in the absence of the zinc foil in the reaction medium.

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