Supporting Information

Diazonium Salt Chemistry for Designing Nano-Textured Anti-Icing Surfaces

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Materials

2 mm thick copper disks were cut in a commercial copper bar. Isopentyl nitrite (117.15 g/mol, Aldrich), 4-heptadecafluoroctylaniline (511g/mol, Aldrich) were used without purification. MilliQ water was used for rinsing the plates and for the preparation of solutions. All the solvents were obtained from Acros organic and used as received.

Preparation of copper surfaces

The copper surfaces were mechanically polished with 0.3 µm Al₂O₃ and rinsed three times under sonication in water. Afterwards, nano-structuration of the copper surfaces was achieved following ref 1. Basically, the surfaces were first dipped in a hydrochloric acid solution for 10 min to remove the native oxide film surface, rinsed with MilliQ water and then immersed into a hot alkaline solution composed of NaClO₂, NaOH, Na₃PO₄·12H₂O and DI water (3.75:5:10:100 wt %) during 5 min at 98 ± 3 °C to form nanostructured CuO. The Cu disks were then rinsed again with deionized water and dried under argon.

Spontaneous grafting of perfluoroalkyl films derived from diazonium salts

The microstructured copper surfaces were functionalized by the in-situ generated aryl diazonium salt in acetonitrile (ACN), as illustrated in Figure S1. For this, the copper disks were immersed in a solution of ACN containing 5mM of 4-heptadecafluoroctylaniline in the presence of isopentyl nitrite (7.5mM). After 24 hours, the modified surfaces were rinsed with copious amounts of water and sonicated in acetone for 5 min.

Figure S1. Description of the procedure to generate the perfluoroalkyl diazonium salt in-situ from 4-heptadecafluoroctylaniline and to graft it on nanostructured copper surfaces.
**Instrumentation**

Scanning Electron Microscope (SEM) images of the different samples were obtained with a Cambridge Supra 40 ZEISS apparatus. The acceleration voltage was set at 5 kV. XPS measurements were performed using a K-Alpha+ system (ThermoFisher Scientific, East-Grinsted, UK) fitted with a micro-focused and monochromatic Al Kα X-ray source (1486.6 eV, spot size: 400 µm). The pass energy was set to 150 and 40 eV for the survey and the high resolution spectra, respectively. The spectra were calibrated against the C—C/C—H C1s component set at 285 eV. The chemical composition was determined by using the manufacturer sensitivity factors using Avantage software, version 5.977. The water contact angles were measured with a Kruss DSA3 instrument. A drop (20 µL) of Milli-Q water was deposited on the top on the sample placed in a horizontal position on the instrument stage. At least, five measurements were made for each sample. The values of the contact angles were calculated by the tangent method using Drop Shape Analysis software.

**XPS results**

1. **Cu2p high resolution spectra**

![Cu2p XPS spectra](image)

*Figure S2.* High resolution Cu2p XPS spectra of (a) bare Cu and (b) nanostructured Cu surfaces.

2. **O1s high resolution spectra**

The O1s core level spectrum of the bare Cu surface shows a large peak at 532.2 eV (see Figure S3) probably due to the presence of adsorbed molecular water. After the surface treatment, two new components appear at 529.9 and 531.6 eV. In comparison with previous investigations on copper surfaces, these binding energies correlate very closely with the expected binding energies of the photoelectrons emitted from CuO and Cu(OH)$_2$. 
Figure S3. High resolution O1s XPS spectra of (a) bare Cu and (b) nanostructured Cu-PF.

3. Auger Cu LMM high resolution spectra
Figure S4 shows the changes observed in the Auger Cu LMM high resolution spectra after the surface treatment. The bare Cu surface displays a main peak centered at 568 eV, due to metallic Cu. After the nanostructuration and functionalization steps, the signal is strongly modified with the appearance of a new component at 570.2 eV, which can be assigned to the formation of Cu(OH)$_2$. The copper(II) oxide layer, CuO, cannot be precisely characterized from the Cu LMM spectrum due to a very small chemical shift of the Cu LMM peak between metallic Cu (~ 568 eV) and CuO (~ 568.5 eV).

Figure S4. Auger Cu LMM high resolution XPS spectra of (a) bare Cu and (b) nanostructured Cu-PF.

Instrument for investigating the anti-icing properties of the surfaces
The anti-icing properties of the copper surfaces were evaluated by measuring the freezing delay time of small droplets (100 μL) cooled down to -20°C starting from an ambient temperature (15 °C) at a constant cooling rate of 1.2°C/min, using an experimental chamber.
maintained at controlled humidity (H=30%) and temperature (see experimental setup in Fig. S5). The freezing process was recorded by an Infrared camera (placed on the top) and CCD (placed on the side). Twenty five measurements were made on each surface. Measurements of the droplet temperature were established by an FLIR A600-series thermographic camera (emissivity fixed at 0.98). The values were provided by the controller with an accuracy of ±0.5 °C.

**Figure S5.** Sketch of the experimental device. A 100 μL drop is deposited onto the substrate at temperature T=15°C. The substrate is cooled down to -20°C starting from +15°C at a constant rate of 1.2°C/min. IR camera (FLIR A600) and visible camera (Imaging Source) are used to view, on the top and on the side respectively, events and record the dynamics of freezing of the sessile drops. This process was repeated 25 times for each sample.

**Comparison of the freezing delay times on bare Cu, planar Cu-PF and Nano Cu-PF measured after several cycles of frosting/defrosting**

**Figure S6.** Delay times of freezing as a function of the number of cycles for bare Cu, planar Cu-PF and Nano Cu-PF surfaces.
Long-term evolution of the water contact angles on Nano Cu and Nano Cu-PF

To analyze the chemical stability of the grafted perfluoroctyl-aryl layers, we have studied the long-term evolution of the contact angle of water droplets deposited onto Nano Cu and Nano Cu-PF (Fig. S7). After a certain time, at 144h, a freezing experiment was performed during which the surface was cooled down to -5°C. This resulted in a jump of the water contact angle for Nano Cu while only a small decrease of the WCA was observed for Nano Cu-PF. The large variation of the WCA observed on Nano Cu after the freezing experiment reveals a poor stability of its surface chemistry. In contrast, Nano Cu-PF surfaces exhibit a long-term superhydrophobic behavior with a WCA higher than 150° after more than 330 h, indicating a high chemical stability of the coating.

Figure S7. Variation of the water contact angle (WCA) with time for Nano Cu (blue columns) and Nano Cu-PF (grey columns). At 144h, a freezing experiment was performed during which the surface was cooled down to -5°C. This resulted in a jump of the water contact angle for Nano Cu while only a small decrease of the WCA is observed for Nano Cu-PF.