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1                   **Superhydrophobic capillary coatings: elaboration,**  
2                   **characterization and application to electrophoretic separations**

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9 **ABSTRACT.**

10 Separation efficiency is ideally controlled by molecular diffusion in capillary electrophoresis  
11 (CE). However, other adverse phenomena, such as solute adsorption on capillary surface, tend  
12 to increase the peak dispersion. An interesting alternative to limit the solute adsorption is to  
13 avoid as much as possible the contact of the solute with the capillary surface by elaborating  
14 superhydrophobic (SH) coatings on fused silica capillary surfaces. This work describes an  
15 optimized protocol to get non-wettable SH coating using hydrophobically modified silica  
16 nanoparticle suspensions (Glaco<sup>TM</sup>), based on simple capillary flushes and thermal  
17 stabilization. In this protocol, the control of the air flushing after the introduction of the  
18 Glaco<sup>TM</sup> suspension in the capillary was found crucial to get optimized coating coverage and  
19 reproducibility. The SH coating was characterized by ellipsometry, atomic force microscopy,  
20 scanning electron microscopy, contact angle (about 159°) and the observation of the meniscus  
21 of water in the coated capillary. The hydrodynamic behavior of the SH coated capillary was  
22 investigated by plotting the Poiseuille law. Finally, electrophoretic separations of a peptide  
23 mixture in acidic conditions demonstrated the interest of this approach with an increase by a  
24 factor 2 of the separation efficiency compared to fused silica capillary.

25

26 **Keywords:** Superhydrophobic coating, wettability, adsorption, capillary electrophoresis.

27

## 28 **1. Introduction**

29 Superhydrophobic surfaces (SHS) are generally generated from the combination of chemical  
30 hydrophobicity with micro and nano-structuration that makes the surface entirely water  
31 repellent. An air layer is formed between the surface and water solution poured on it. The  
32 most well-known examples can be found in Nature with lotus leaves, butterfly wings, petals  
33 of rose, or legs of gerris [1-3]. Direct applications of SHS include self-cleaning, antifreeze,  
34 anticorrosion, and anti-friction surfaces, together with droplet handling [1-3]. Other  
35 applications exist in pharmaceutical and biomedical fields, such as the study of cellular  
36 communication or the reduction of bacterial adhesion on biomedical implants [4].

37 HS can be characterized by the measurement of the static contact angle (CA), which is the  
38 macroscopic angle between the solid-liquid interface and the liquid-air interface when a water  
39 droplet is deposited on a solid surface. The higher the CA value, the more spherical the  
40 droplet is, and so, the more repellent to water the surface is. A surface is hydrophilic when  
41  $CA < 90^\circ$ , while it is considered as hydrophobic when  $90^\circ < CA < 120^\circ$ , and  
42 superhydrophobic when  $CA > 120^\circ$  [5].

43 SHS can be divided into two categories with antagonistic effects. The lotus effect  
44 prevents water molecules from adhering to the surface, while the petal effect corresponds to a  
45 sticking (but non-wetting) water drop on the surface. The difference between these two  
46 categories is generally related to pattern periodicity and surface roughness [2]. Apart from  
47 these two effects, surface wetting on SHS can be characterized by the so-called Cassie (non-  
48 wetting) [6] and Wenzel (wetting) states (Figure 1). In the Cassie state, air bubbles are present  
49 in the anfractuosités of the surface, while the liquid fill most of the space in the Wenzel state  
50 [7-8]. Some SHS can lead to slippage (Cassie state with a lotus effect), others not (Cassie  
51 state with a petal effect). In this context, Wenzel state corresponds to simple hydrophobic  
52 wetting. Due to the presence of air, water friction on SHS is reduced and generally

53 characterized by the slip length that is defined as the length corresponding to the intercept  
54 along the axis orthogonal to the interface when a tangent line is drawn along the velocity  
55 profile at the interface [9-11].

56 SHS can be prepared in several ways that are generally based on silica nanoparticles,  
57 carbon nanotubes, SU-8 polymeric photoresist, polydimethylsiloxane (PDMS) or lithography  
58 [12]. For instance, microchannels (30  $\mu\text{m}$  deep x 300  $\mu\text{m}$  wide x 8 cm long) coated by  
59 octadecyltrichlorosilane (OTS), give a CA of  $120^\circ$  and 0.92  $\mu\text{m}$  slip length [13]. Other  
60 examples can be found in the literature. Lotus-leaf layered columns (7 to 19 mm diameter,  
61 145 mm height) were obtained by lotus leaf print on flat flexible cellophane paper (100  $\mu\text{m}$   
62 thick) and then filled with steel balls of 4.6 mm diameter, giving a CA higher than  $150^\circ$  and  
63 47-117  $\mu\text{m}$  slip length [14]. Cylindrical microchannels (150  $\mu\text{m}$  diameter) were prepared with  
64 negative print of lotus leaf surface in polystyrene, giving a CA of  $160^\circ$  [15]. Microchannels  
65 were coated with carbon nanotubes, giving a CA of  $165^\circ$  and 20  $\mu\text{m}$  slip length [16].  
66 Superhydrophobic cells consisting of two surface-modified glass plates with nanostructured  
67 silica wall (by deposition of soot, tetraethoxysilane and alkyl trichlorosilane layers) were used  
68 with two platinum electrodes, giving a CA of  $169^\circ$ , less than 1  $\mu\text{m}$  roughness, up to 30 nm  
69 slip length under 0 to 50 V/cm electrical field, but no increase of electroosmotic flow [17].

70 Capillary electrophoresis (CE) is a separation technique especially well-suited for the  
71 analysis of (bio)macromolecules such as peptides, proteins and polysaccharides. In the ideal  
72 case, when separation efficiency is controlled by molecular diffusion, the theoretical plate  
73 number in CE is inversely proportional to the molecular diffusion coefficient [18-21].  
74 Therefore, the larger the solute is, the lower its molecular diffusion coefficient, and the higher  
75 the separation efficiency. However, other dispersive phenomena can occur, such as solute  
76 adsorption onto the capillary wall, which tend to decrease the separation efficiency [22]. In  
77 order to minimize protein adsorption, capillaries can be physically or chemically coated with

78 a neutral [23] or charged polymer [24] or even using polyelectrolyte multilayers [25][26].  
79 Njoya et al. proposed the use of silica colloidal crystals (with ordered arrangements of silica  
80 spheres coated with polyacrylamide) for protein electrophoresis leading to plate height of only  
81  $0.15\ \mu\text{m}$  [27]. An interesting alternative to avoid solute adsorption onto the capillary wall  
82 would be to limit the wettability of the water-based electrolyte onto the capillary surface. To  
83 our knowledge, the idea of using SHS in CE has not been yet investigated. When hydrophobic  
84 surfaces are used in CE or miniaturized chip electrophoresis [17, 28-31], researchers generally  
85 try to reduce the analyte adsorption by modifying/coating the capillary/channel wall and  
86 making them more hydrophilic. For instance in ref [30], electrophoretic separations of amino  
87 acids were compared in PDMS microchannels without and with an in situ polyethylene glycol  
88 covalent modification using air-plasma treatment and silanization [30]. Coated PDMS  
89 microchannels gave much better separation efficiency (up to 20 times) due to higher  
90 hydrophilicity leading to lower CA ( $64^\circ$  instead of  $106^\circ$  for non-coated PDMS). In this work,  
91 we propose a paradigm change by making the capillary wall so hydrophobic that the capillary  
92 surface should become unwettable by the background electrolyte, and by the solute zone. By  
93 this way, the interactions between the solutes and the capillary wall should be reduced.  
94 Finally, it is worth noting that slip flow occurring in chromatography using colloidal crystals  
95 made of 470 nm silica spheres that are chemically modified with hydrocarbon considerably  
96 enhance the separation efficiency [32].

97 Glaco<sup>TM</sup> is a commercial isopropyl alcohol suspension containing hydrophobically  
98 modified silica nanoparticles used as a spray to make car windshields and wing mirrors  
99 superhydrophobic to improve visibility during rainy conditions. Glaco<sup>TM</sup> coating has been  
100 used and reported in literature based on a simple coating protocol consisting in the contact of  
101 the surface to be treated with the Glaco<sup>TM</sup> solution, followed by heating at  $200^\circ\text{C}$  for 30 min  
102 [33]. This process was generally repeated 3-4 times [33]. **Atomic Force Microscopy (AFM)**

103 studies of the Glaco™ treated surface showed that particle size was about 30 to 50 nm, with  
104 50 to 200 nm roughness, a CA of minimum 155° and a sliding angle less than 5° [33-34].  
105 Superhydrophobicity was observed on Glaco™ treated microscope glass blade (with receding  
106 angle of 150° and advancing angle of 164°) [35].

107 This work aims at elaborating, characterizing and using superhydrophobic coatings in  
108 fused silica capillaries using Glaco™ deposition for electrophoretic separations.

109

## 110 **2. Experimental section**

### 111 **2.1. Chemicals and samples**

112 Glaco Mirror Coat Zero™ was purchased from Soft99 (Osaka, Japan). It is made of silica  
113 nanoparticles (hydrophobically modified with alkyl functions) suspension in isopropyl alcohol  
114 (see Material safety data sheet [36]). The nanoparticle concentration in the Glaco™ solution is  
115 about 4 g/L, as quantified by weighting the dry residue after evaporation of the solvent.  
116 Ultrapure grade water (18 MΩ.cm) was produced on a Milli-Q equipment (Merck Millipore,  
117 USA). Sodium hydroxide (NaOH) and N,N-dimethylformamide (DMF, 99% m/m) were  
118 purchased from Sigma-Aldrich (St Quentin Fallavier, France). 4-(2-hydroxyethyl)-1-  
119 piperazine ethanesulfonic acid (HEPES) from VWR (Fontenay-sous-bois, France),  
120 tris(hydroxymethyl)aminomethane (Tris) from Thermo Fischer (Karlsruhe, Germany) and  
121 sodium phosphate, monobasic 99% m/m from Aldrich Chemical Company (Milwaukee,  
122 USA) were used as received to prepare the different background electrolytes in CE.  
123 Creatinine, alanine dimer (Ala-Ala), alanine trimer (Ala-Ala-Ala), alanine tetramer (Ala-Ala-  
124 Ala-Ala), Lys-His-Gly and Bursin tripeptides were purchased from Sigma-Aldrich (Saint-  
125 Quentin Fallavier, France). Brilliant Blue FCF (food coloring, E133) was used as a water  
126 colorant purchased from Vahiné (Avignon, France) and used as is.

### 127 **2.2. Glaco™ coating**

128 Glass blades (76 x 26 mm, Thermo Scientific, Germany) were coated with Glaco™ by  
129 pouring Glaco™ solution on them using a 5 mL plastic pipette. Isopropyl alcohol was then  
130 evaporated and the coating was stabilized by placing the glass blades in an oven for 15

131 minutes at 250°C. The same process was repeated 3 times to obtain maximum covering of the  
132 glass surface by the Glaco™ nanoparticles.

133 Fused silica capillaries (PolyMicro Technologies, Photonlines, Saint-Germain-en-  
134 Layes, France) of 360 µm external diameter, various internal diameters (180, 100 and 50 µm),  
135 and 40 cm total length (30 cm to the detector window) were coated with Glaco™ by flushing  
136 at a given pressure and for a given duration that depended on the internal diameter (see Table  
137 1). Excess of Glaco™ solution was removed by flushing with air at a well-defined pressure /  
138 duration depending on the capillary internal diameter (I.D.) (see Table 1). Coating was then  
139 thermally stabilized by placing the capillaries in a GC-2010 Plus oven (Shimadzu, Marne-la-  
140 Vallée, France) for 15 min at 250°C without any gas flow. The same process was repeated 4  
141 times by alternating the flushing direction in the capillary (alternatively from the starting or  
142 the ending ends of the capillary) to obtain maximum covering of the capillary walls by the  
143 Glaco™ nanoparticles. Capillaries were finally let overnight under ambient air at room  
144 temperature before use.

145

## 146 **2.3. Surface characterization methods**

### 147 **2.3.1 Contact Angle (CA)**

148 Contact angle between droplets of 20 mM HEPES + 10 mM NaOH (pH 7.46) solution and  
149 Glaco™ treated glass blades was measured using PAT tensiometer (Sinterface, Berlin,  
150 Germany). Dropsnake plugin on ImageJ software was used for processing the picture of the  
151 droplet. Advancing contact angle was measured by growing gradually (with 1 µL steps) the  
152 droplet volume from 20 µL to 30 µL, while receding angle was measured by decreasing  
153 gradually the droplet volume from 30 µL to 20 µL.

### 154 **2.3.2 Ellipsometry**

155 Multiple angles of incidence ellipsometry (Multiskop Optrel, Sinzing, Germany) was used to  
156 measure the thickness  $d_{Glaco}$  and refraction index  $n_{Glaco}$  of the Glaco™ coating on a glass blade  
157 and the thickness of the air layer on a Glaco™ coated glass blade submerged in deionized  
158 water. The incidence angle of the laser beam (533 nm) could be finely modified and the  
159 reflected polarized light was detected by a four quadrant photodiode (2×2 cm<sup>2</sup>). Ellipsometry  
160 at the water-solid interface was measured by using light guides immersed in water in order to

161 detect the reflection from the water-solid interface avoiding the reflection coming from the  
162 air-water interface [37].

### 163 **2.3.3 Atomic Force Measurement (AFM)**

164 Tapping Mode Atomic Force Microscopy (TM-AFM) images were acquired with a Bruker  
165 Nanoman (Bruker SAS, Palaiseau, France) driven by Nanoscope 3A Quadrex electronics. The  
166 cantilever tips were Silicon Point Probe Plus<sup>TM</sup> NCSTR (Nanosensors, Neuchâtel,  
167 Switzerland) used at a constant force of 6.5 N/m, resonance frequency of 157 kHz. All the  
168 image treatments and the thickness measurements were performed using WSxM 4.0 Beta 8.2  
169 and the resulting data were treated with the Fityk software to correct the background of the  
170 image.

### 171 **2.3.4 Dynamic Light Scattering (DLS)**

172 Glaco<sup>TM</sup> nanoparticles size was measured with a Litesizer<sup>TM</sup> 500 (Anton Paar, Graz, Austria)  
173 dynamic light scattering (DLS) equipment mounted with a BM10 module, driven by Kalliope  
174 1.8.4 software. Quartz cells (10 mm x 10 mm x 45 mm) were used. Refraction index of  
175 isopropyl alcohol was 1.3749 at 25 °C. Transmittance was 98.3% at 90°. Glaco<sup>TM</sup> solution (4  
176 g/L in nanoparticle) was used as received for the DLS measurement.

### 177 **2.7. Scanning Electron Microscopy (SEM)**

178 Scanning Electron Microscopy (SEM) was realized using a Hitachi S4800 machine (Hitachi  
179 High Technologies America, Inc., Schaumburg, Illinois, USA). Thickness, roughness and  
180 nanoparticle size were measured on Glaco<sup>TM</sup> coated glass blades and capillaries. Inner surface  
181 of capillaries were made accessible to SEM by burning the external polyimide protection  
182 layer of the capillaries and then by shattering it with a ceramic capillary cutter on a double  
183 faced tape support to obtain some shards turned face up. Acceleration voltage varied from 0.1  
184 to 30 kV depending on the magnification and sample conductivity.

### 185 **2.3.6 Optical Microscopy**

186 USB optical microscope n° 44302 (Celestron, California, USA) was used to observe the  
187 capillary wall-air-electrolyte interface in Glaco<sup>TM</sup> coated capillaries at ×150 magnification.  
188 Capillaries (40 cm total length) of various internal diameters (50, 100 and 180 µm) were



189 observed after being partially filled with brilliant blue dyed water (1 g/L) and air bubble.  
190 Dyed water and air were introduced with a syringe fixed on capillary by a LuerTight™ 360  
191 µm outside diameter (O.D.) tubing to Luer connection (P-662 rapid connection, IDEX Health  
192 and Science, California, USA).

### 193 **2.3.7. C4D profiling of the Glaco™ coated capillary**

194 The capacitively coupled contactless conductivity detector (C4D) was a TraceDec  
195 (Innovative Sensor Technologies GmbH, Innsbruck, Austria) used with the following settings:  
196 frequency 2xHIGH, voltage -12 Db, gain 50% and offset 0. Conductivity measurements were  
197 performed along the capillary under a 1 mL/min flow rate of 20 mM HEPES + 10 mM NaOH  
198 electrolyte, pH 7.46. The flow rate was ensured by a syringe-pump (KD Scientific, USA)  
199 connected to the capillary by a LuerTight™ connection (P-662 rapid connection, IDEX Health  
200 and Science, California, USA). The C4D cell was moved along the capillary by steps of 3 cm,  
201 and the conductivity was measured at each point. Fused silica capillaries of different I.D. were  
202 tested as reference and compared to a 100 µm I.D. Glaco™ coated capillary.

203

### 204 **2.3.8. Hydrodynamic behavior: Poiseuille law**

205 The flow rate under given hydrodynamic pressure was measured using the CE  
206 equipment on Glaco™ coated capillaries and fused silica capillaries (40 cm total length, 30  
207 cm to detector) of three different I.D. (50, 100 and 180 µm), by applying different pressures  
208 with the 20 mM HEPES + 10 mM NaOH electrolyte, pH 7.46, containing 0.5% v/v DMF as  
209 UV marker. Between each run, the capillary was flushed by the same background electrolyte  
210 (BGE), without UV marker, at a given pressure depending of the capillary I.D. (3 psi 2 min  
211 for I.D. 100 µm, 10 psi 5 min for I.D. 50 µm, and 1 psi 2 min for I.D. 180 µm. 1 psi = 0.06  
212 bar). For 50 µm (resp. 100 µm and 180 µm) I.D. capillaries, applied pressure range was 3 to

213 14 psi (resp. 1 to 3 psi and 0.2 to 1.2 psi). Detection of the marker was monitored by UV  
214 absorbance at 190 nm. Flow-to-pressure relationship was used to calculate the apparent  
215 capillary diameter, and to estimate the slip length.

216 The flow rate  $Q$  (in  $\text{m}^3/\text{s}$ ) at a given pressure  $\Delta P$  (in Pa) was calculated from the  
217 detection time  $t_{DMF}$  (in s) of the DMF marker according to:

$$218 \quad Q = \frac{l\pi R_c^2}{t_{DMF}} \quad (1)$$

219 where  $l$  is the length of the capillary to the UV detection window and  $R_c$  is the capillary  
220 radius. Poiseuille law ( $Q$  vs  $\Delta P$ ) was systematically plotted. The slope  $a$  of the  $Q$  vs  $\Delta P$   
221 relationship depends on the apparent radius  $R_e$  of the capillary, according to the following  
222 equation:

$$223 \quad Q = \frac{\pi R_e^4 \Delta P}{8\eta L} \quad (2)$$

224 where  $\eta$  is the viscosity of the solution (in Pa.s) and  $L$  is the total length of the capillary (in  
225 m). It is therefore possible to determine the apparent radius  $R_e$  from the slope  $a$  using the  
226 following equation:

$$227 \quad R_e = \left( \frac{8\eta L a}{\pi} \right)^{1/4} \quad (3)$$

### 228 **2.3.9. Capillary electrophoresis**

229 Capillary electrophoresis experiments were carried out on a P/ACE™ MDQ  
230 Beckman-Coulter (Sciex, Villebon sur Yvette, France) piloted by 32 Karat software. Bare  
231 silica and Glaco™ coated capillaries of various internal diameter (I.D.), and of total capillary  
232 length 40 cm and effective capillary length 30 cm, were tested for the electrophoretic  
233 separation of peptides mixtures. Unless otherwise specified, all electrolytes were prepared  
234 with boiled ultrapure water to obtain gas-free solutions. Electrophoretic separations were

235 performed in a Tris / Phosphate 6.5 mM / 14.1 mM electrolyte at pH 2.5 (10 mM ionic  
236 strength). Before each run the capillary was flushed at 3 psi for 2 min (I.D. 100  $\mu$ m). Peptides  
237 mixture for analysis (0.1 g/L in water of Lys-His-Gly, Arg, creatinine, Ala, Ala-Ala and Ala-  
238 Ala-Ala) was injected into the capillary at 0.2 psi, 2 s (1.06 nL for a capillary of 50  $\mu$ m I.D.).  
239 Separations were realized at 10 kV with a pressure of 3 psi at both capillary ends of the  
240 capillary to stabilize the electrical current. Between each run, the capillary was flushed by the  
241 BGE at a pressure depending of the capillary I.D. (3 psi 2 min for I.D. 100  $\mu$ m, 10 psi 5 min  
242 for I.D. 50  $\mu$ m, and 1 psi 2 min for I.D. 180  $\mu$ m). The temperature of the capillary cartridge  
243 was set at 25°C. UV detection was performed at 214 nm. Separation efficiency was  
244 determined using the following equation:

$$245 \quad N = 5.54 \left( \frac{t_m}{\delta} \right)^2 \quad (4)$$

246 where  $t_m$  is the migration time and  $\delta$  is the half-height peak width determined using CEval 0.6  
247 software available at the following address [<https://echmet.natur.cuni.cz/software/ceval>].

### 248 **3. RESULTS AND DISCUSSION**

#### 249 **3.1. Superhydrophobic glass blade**

250 Glaco™ coated glass surfaces were first prepared on glass blades, based on simple contact  
251 of Glaco™ solution on the surface followed by a heating treatment at 250°C, both repeated  
252 three times (see the experimental protocol described in the experimental part). Figure 2  
253 displays a picture of a ~20  $\mu$ L water droplet deposited on the Glaco™ coated glass surfaces.  
254 A static contact angle (CA) of 159° ( $\pm$  6°, which is the standard deviation based on  $n= 4$   
255 repetitions on 3 different blades) was observed for advancing droplet (i.e. growing droplet)  
256 and 145° ( $\pm$  12°) for receding (i.e. decreasing droplet size), clearly demonstrating that  
257 Glaco™ coated glass blades present superhydrophobic behavior (defined as CA > 120°).  
258 Figure SII shows a photography of an immersed glass blade and the air layer covering it. The

259 silver-mirror sheen of the immersed coated glass blade is due to a thin air layer retained on the  
260 surface, and is the signature appearance of Cassie state [34].

261 To better characterize the surface, the thickness of the Glaco<sup>TM</sup> layer and of the air layer  
262 between the immersed Glaco<sup>TM</sup> coated glass surface and water were measured by  
263 ellipsometry (Figure 3). Uncoated glass blade in contact of water shows the absence of an air  
264 layer at the solid-liquid interface (Figure 3A). Figure 3A shows scans of the ellipsometric  
265 amplitude ( $\tan\Psi$ ) and phase ( $\Delta$ ) as a function of the incident angle ( $\varphi$ ) for a bare and a  
266 Glaco<sup>TM</sup> coated glass surfaces exposed to air. Around the Brewster angle ( $\varphi_{Br}=\arctan(1/n_{Glass}=56.8)$ ),  $\tan\Psi$  and  $\Delta$  change sharply for the uncoated surface confirming the  
267 absence of an interfacial layer and the cleanness of the glass substrate. In the presence of a  
268 Glaco<sup>TM</sup> coating,  $\tan\Psi$  and  $\Delta$  deviate strongly from the ones of the bare surface, which allows  
269 us to evaluate the average thickness and refractive of the coating:  $n_{Glaco}=1.58\pm0.1$  and  
270  $d_{Glaco}=270\pm5$  nm (see inset of Figure 3), assuming a single layer interfacial profile between  
271 two macroscopic media: water and air. Ellipsometry was also performed for glass blades in  
272 water, as shown in Figure 3B. In order to fit these results, we introduce an additional  
273 interfacial layer of refractive index  $n_{Air}$  and thickness  $d_{Air}$ , fixing the refractive index of the  
274 glass substrate  $n_{Glass}$  and the thickness of the Glaco<sup>TM</sup> coating (as obtained from Figure 3A).  
275 From the fits, we obtain  $n_{Air}=1.17-1.24$  and thicknesses  $d_{Air}=124-208$  nm. Being  $n_{Air} < n_{Water}$   
276  $= 1.333$ , we can interpret this result as the observation of gas bubbles trapped in water on the  
277 hydrophobic Glaco<sup>TM</sup> surface. The interfacial layer between water and the Glaco<sup>TM</sup> coating  
278 could be modelled as a mixed layer composed by gas bubbles immersed in water. The volume  
279 fraction of air  $f$  in the interfacial layer of thickness  $d_{Air}$  could be evaluated accounting for the  
280 Wiener effective medium approximation [38]:  
281

$$282 \quad n_{Air}^2 = f + (1 - f)n_{Water}^2 \quad (5)$$

283 which leads to  $f = 0.31-0.52$  .

284 Figure 4 displays the surface topology of the Glaco™ onto the glass blade as observed by  
285 AFM (tapping mode). Excellent coverage of the surface was observed, with a thickness of  
286 about 200 nm (Figure 4A and 4B). Particle size was about 30 nm (Figure 4C) and roughness  
287 was about 100 nm (Figure 4B). Granulometric distribution of the Glaco™ solution (in  
288 isopropyl alcohol) measured by DLS showed an intensity average hydrodynamic diameter of  
289 135 nm (with a polydispersity index of 23%). Glaco™ suspension is made of stable raspberry  
290 shaped clusters of smaller nanoparticles (~30 nm diameter) as shown in Figure 4C. These  
291 results are in agreement with a self-similar fractal structure [39]. Neither ultrasounds, nor  
292 dilution, were found to modify cluster size (monitored by DLS).

293

### 294 **3.2. Superhydrophobic capillary coating**

295 Glaco™ coated capillaries were then prepared according to an optimized protocol described  
296 in the experimental part. In brief, this protocol is based on the 4-times repetition of a three  
297 steps procedure based on: (i) flushing of the capillary with the Glaco™ suspension; (ii)  
298 controlled air flushing of the capillary leading to a Glaco™ film deposition onto the capillary  
299 surface and (iii) the thermal stabilization of the coating at 250°C in a GC oven. Step (ii) was  
300 found to be crucial to control the quantity of Glaco™ deposited onto the capillary surface.  
301 The thickness ( $\varepsilon$ ) of the Glaco™ film remaining on the fused silica capillary when flushing  
302 with air strongly depends on the applied air pressure to remove the Glaco™ suspension, as  
303 shown by equation (6) from the Landau, Levich and Derjaguin (LLD) theory (also known as  
304 the Bretherton law)[40] :

$$305 \quad \varepsilon = 1.34R_c Ca^{2/3} \quad (6)$$

306 where  $Ca$  is the dimensionless capillary number defined by equation (7):

$$307 \quad Ca = \frac{\eta V}{\gamma} \quad (7)$$

308  $\gamma$  is the surface tension of the coating solution (in N/m) and  $V$  is the linear velocity of the  
309 coating solution flushed by air pressure (in m/s). Combining equations (6), (7) with the  
310 Poiseuille law leads to:

$$311 \quad \varepsilon = 1.34R_c^{7/3} \left( \frac{\Delta P}{8L\gamma} \right)^{2/3} \quad (8)$$

312 where  $\Delta P$  is the applied pressure at which the air replace the Glaco™ solution, and  $L$  is the  
313 capillary length. It is worth noting that equations (6) and (8) are only valid for  $Ca$  lower than  
314  $10^{-2}$ . The pressure  $\Delta P$  were adjusted so that the coating thickness was similar for all capillary  
315 I.D.. Taking  $\gamma = 0.0217$  N/m at 20°C for isopropyl alcohol (solvent of Glaco™ suspension),  
316 and the  $\Delta P$  values set in Table 1 for each capillary I.D., leads to Glaco thickness  $\varepsilon = 1.1, 1.2$   
317 and  $1.0 \mu\text{m}$  for capillary I.D. of 50, 100 and 180  $\mu\text{m}$ , respectively.  $Ca$  numbers are  $5.9 \times 10^{-3}$ ,  
318  $2.3 \times 10^{-3}$ ,  $7.6 \times 10^{-4}$  respectively, demonstrating the validity of equation (8). Following this  
319 experimental protocol, very good coating coverage of the capillary inner wall surface was  
320 observed, as shown by scanning electron microscopy (SEM) in Figure 5, even if the surface  
321 coverage was found less effective in capillaries (Figure 5C to 5F) than in glass blade (Figure  
322 5A).

323 Scanning contactless conductivity detector (sC4D) was next used to sense the capillary  
324 inner surface (as discussed in a review paper [41]) by measuring the conductivity at different  
325 positions along the capillary under constant flow rate with a 20 mM HEPES electrolyte (pH  
326 7.46). The conductivity measurements confirm that the thickness of the glaco coating is  
327 negligible compared to the capillary I.D., as the conductivity was similar on Glaco™ coated  
328 and on a fused silica capillaries (see Figure SI2).

329 To demonstrate that the superhydrophobicity was also observed inside the capillaries (and  
330 not only on the coated glass blades), the meniscus of a blue colored water solution injected in  
331 Glaco™ coated capillaries was compared to the one observed in a fused silica capillary  
332 (Figure 6). As expected for a SHS, the meniscus was reversed in the case of Glaco™ coated

333 capillaries for all internal diameters (50, 100 and 180  $\mu\text{m}$  I.D.). It is worth noting that flushing  
334 the capillary with air by hand using a syringe and LuerTight™ connector in step (ii) of the  
335 coating protocol did not give reversed meniscus (only flat profile of the interface; not shown).  
336 Similarly, using lower pressure in step (ii) that those given in Table 1, leads to thinner film  
337 deposition ( $< 1 \mu\text{m}$ ) and weaker SH properties.

338

### 339 **3.3. Hydrodynamic behavior**

340 Before studying the hydrodynamic behavior (Poiseuille law), it was first observed that a  
341 minimal pressure of 0.3 psi was required to flush a freshly prepared 180  $\mu\text{m}$  I.D. Glaco™  
342 coated capillary, initially filled with air, with a HEPES / Na BGE. Below that limiting value,  
343 the BGE did not enter in the capillary. This is in good agreement with the minimum pressure  
344 predicted by the Young-Laplace law:

$$345 \quad P_{\min} = \frac{2\gamma}{R_c} \quad (9)$$

346 with  $\gamma = 72 \text{ N/m}$ ,  $R_c = 90 \mu\text{m}$ , leading to  $P_{\min} = 0.23 \text{ psi}$ . This experimental observation is in  
347 agreement with the SHS of the Glaco™ coated capillary.

348 Figure 7A displays the BGE fronts (0.5% v/v DMF was added in the BGE as a marker)  
349 obtained at different applied pressures in Glaco™ coated capillaries, initially filled with  
350 HEPES / Na BGE at 1 psi 2 min, and in fused silica capillary for comparison (all capillaries  
351 with 180  $\mu\text{m}$  I.D.). The higher the applied pressure, the shorter the elution time. Flow rates  
352 were plotted against the applied pressure (Figure 7B). The slope is directly related to the  
353 apparent capillary radius,  $R_e$ , that can be determined using equation (3). The blue trace in  
354 Figure 7B corresponds to the behavior of a fused silica capillary, leading to an effective radius  
355 of 94  $\mu\text{m}$  which is very close to the expected value of 90  $\mu\text{m}$ , assuming no-slip boundary  
356 conditions at the silica surface. As for the superhydrophobic 180  $\mu\text{m}$  I.D. Glaco™ coated  
357 capillary, it was first observed a shift in the Poiseuille law with a pressure drop of about 0.3

358 psi (or 2100 Pa, yellow trace in Figure 7B), which is due to the presence of multiple air  
 359 bubbles in the capillary. Using equation (9), we can estimate that a bubble separating two  
 360 plugs of BGE in a 180  $\mu\text{m}$  I.D. capillary generate a pressure drop  $\Delta P_{bubble}$  of  $\sim 100$  Pa taking  $\gamma$   
 361  $= 72$  N/m,  $R_c = 90$   $\mu\text{m}$ ,  $\theta_r = 145^\circ$  and  $\theta_a = 160^\circ$ :

$$362 \quad \Delta P = \frac{\gamma}{R} (\cos(\theta_r) - \cos(\theta_a)) \quad (10)$$

363 This observation means that the pressure drop would correspond to a train of approx. 20  
 364 bubbles in the whole capillary. Experimentally, using a USB optical microscope, 14 to 24  
 365 bubbles could be observed in the Glaco™ coated capillary, in good agreement with the  
 366 expectations.

367 The Poiseuille law measurements was duplicated one week later on the same capillary,  
 368 leading to the red trace with apparent slippage (slope higher than bare silica slope)  
 369 corresponding to a slip length of 23.3  $\mu\text{m}$ , calculated from the Poiseuille law corrected from  
 370 the slip length factor [42] leading to:

$$371 \quad b = \frac{2\eta La}{\pi R^3} - \frac{R}{4} \quad (11)$$

372 with  $b$  the slip length and  $a$  the slope of the Poiseuille profile (i.e.  $Q/\Delta P$ ). The poor linearity of  
 373 the Poiseuille law at low flow rate can be explained by unstable flows (i.e. the flow can be  
 374 temporally stopped), leading to non-linear behavior.

375 Finally, the same experiments performed one week later, leads to the green trace, which is  
 376 similar to the fused silica capillary. These observations are in agreement with a progressive  
 377 coating degradation that led to the loss of the meniscus inversion upon time. The fact that the  
 378 slipping behavior (higher slope in the Poiseuille law than for fused silica capillary) was  
 379 observed at intermediate state (in week 2), could be related to the pattern and the density of  
 380 the Glaco™ coating, which is affected by the progressive coating degradation. Indeed, it was  
 381 shown recently that the effective slip length strongly depends on the meniscus angle  $\theta_{meniscus}$



382 of the nanobubble trapped between the surface anfractuosités and the liquid (see e.g. Figure 3  
383 in ref. [43]). In the Cassie regime, when bubbles fill the holes,  $\theta_{meniscus}$  between  $-30^\circ$  and  $45^\circ$   
384 leads to positive slip length with a maximum slip at  $\sim 0^\circ$ . For  $\theta_{meniscus} > 45^\circ$ , the slip lengths  
385 become negative, i.e. smaller than in the Wenzel case (without any gas phase trapped on the  
386 surface = no slip). Negative effective slip lengths can be explained by an immobilized layer of  
387 the liquid close to the wall. In this limit, the liquid–solid friction is higher than on a non-  
388 slipping surface (without holes) [43]. We can imagine that the freshly prepared Glaco™ SHS  
389 leads to high  $\theta_{meniscus}$  ( $>45^\circ$ ) with no slipping surface. Then, the aging of the coating may  
390 favor the formation of less protruding gas bubbles and the slip condition at the SHS surface  
391 occurs (ideal metastable Cassie slipping state), before recovering a more classical no-slip  
392 condition (Wenzel state), leading to similar hydrodynamic behavior as observed on silica  
393 surface.

394 Similar results were obtained on 100  $\mu\text{m}$  and 50  $\mu\text{m}$  I.D. Glaco™ coated capillaries (see  
395 Figures SI3 and SI4), even if the intermediate slipping state was not observed; probably  
396 because it is metastable.

397 To get more insight on the reason of the coating degradation upon time, and to investigate if  
398 the degradation was caused by the mechanical erosion due to the capillary flushing between  
399 hydrodynamic experiments (1 psi  $\sim$ 70 mbar, 2 min), a freshly coated capillary was left in the  
400 HEPES / Na pH 7.5 BGE to see if the meniscus was lost with time in absence of capillary  
401 flushing. The meniscus starts to be altered after 4 to 7 days (see Figure SI5 for more details),  
402 while the SHS was conserved even after 18 days of contact with a Tris / Phosphate pH 2.5  
403 BGE. This is why the pH 2.5 BGE was used to study the electrokinetic behavior.

404

### 405 **3.4. Electrokinetic Behavior of SHS coated capillaries**

406 Freshly prepared 100  $\mu\text{m}$  I.D. Glaco™ coated capillaries were used to separate a peptide  
407 mixture composed of Bursin, Lys-His-Gly, creatinine, Ala-Ala, Ala-Ala-Ala and Ala-Ala-  
408 Ala-Ala in acidic conditions (Tris / Phosphate 6.5 mM / 14.1 mM at pH 2.5). Separation  
409 efficiencies were compared with those obtained on a fused silica capillary in the same  
410 conditions. Figure 8 shows the electrophoregrams and the corresponding current intensity  
411 obtained using the fused silica capillary (Figure 8A) and the Glaco™ coated capillary at  
412 different times (Figure 8B to 8E).

413 Separations could not be obtained on the freshly prepared Glaco™ coated capillaries (Figure  
414 8B) with reversed meniscus (see insert in Figure 8B), due to unstable current intensity  
415 probably because of the presence of large air bubbles in the capillary. This phenomenon was  
416 observed despite the degassing of the BGE (using boiled water) and the application of a +3  
417 psi pressure on both ends of the capillary to help to stabilize the current intensity. After 5  
418 runs, the meniscus was less reversed, and stable separations could be obtained with +3 psi  
419 pressure (Figure 8C). Figure 9 gives the separations efficiencies (in plate number) obtained on  
420 a fused silica capillary (blue) and on three different Glaco™ coated capillaries. Much better  
421 separation efficiencies were obtained on Glaco™ coated capillaries (up to 60 000 plates)  
422 compared to fused silica capillary (less than 25 000 plates). These results were reproducible,  
423 as shown by the data reported on 3 different Glaco™ coated capillaries. These encouraging  
424 results demonstrate that a low wettability of the capillary surface can increase the separation  
425 efficiency (with an average gain by a factor 2 on the separation efficiency). However, the  
426 stabilization of the current intensity is difficult to obtain on freshly SHS due to air bubble  
427 formation.

428 Increasing the total number of runs leads to some coating degradation as demonstrated by the  
429 shape of the meniscus (see Figures 7C to 7E), which tends to become flat (Figure 7D), or not  
430 well defined (Figure 7E), probably because of the occurrence of coating heterogeneities. This

431 degradation tends to increase the peak dispersion, and thus, to decrease the separation  
432 efficiencies. It is worth noting that a progressive wetting of the surface leading to the Wenzel  
433 state, instead of a coating degradation, was discarded since the SH state was not recovered  
434 after heating of the degraded capillary in a GC oven at 250°C for 15 min.

435 Coming back to freshly prepared SHS capillaries, the +3 psi stabilization pressure (both ends)  
436 used to try to stabilize the current intensity was arbitrarily chosen. Conceptually, it only had to  
437 be lower than  $P_{lim}$ , the pressure above which wetting of the coating is forced by the  
438 compression of the air bubble. This limiting pressure value  $P_{lim}$  was evaluated to be ~100 psi  
439 (7.1 bars) using equation (12):

$$440 \quad P_{lim} = \frac{\gamma}{r} \quad (12)$$

441 taking  $\gamma$  the superficial tension of the BGE ( $72 \times 10^{-3}$  N/m), and  $r$  the roughness of the  
442 capillary wall (100 nm, see AFM measurement). Stabilization pressures higher than 3 psi  
443 were tested (up to 80 psi), but none of those tests gave better results regarding current  
444 stabilization (or separation efficiency) compared to the application of 3 psi. The current  
445 intensity was not stabilized faster (there were still approx. 5 runs similar to Figure 8B before  
446 the capillary behavior was similar to figure 8C).

447

#### 448 **4. CONCLUSION**

449 In this work, we report for the first time a simple coating protocol to obtain superhydrophobic  
450 coatings in fused silica capillaries with I.D. comprised between 50  $\mu\text{m}$  and 180  $\mu\text{m}$ . The  
451 pressure of the air flush to remove the Glaco<sup>TM</sup> coating suspension was found to be crucial to  
452 control the thickness, the homogeneity and the reproducibility of the coating layer. The  
453 coating layer was ~200-300 nm thick, with 100 nm roughness and ~100-200 nm air layer  
454 when dipped in water. SHS were obtained in the 50-180 $\mu\text{m}$  I.D. fused silica capillaries as  
455 demonstrated by the shape of the meniscus and the existence of a limiting pressure to

456 introduce water in a capillary previously filled with air. The hydrodynamic behavior of the  
457 superhydrophobic capillaries revealed the presence of air bubbles in the capillary, as observed  
458 optically and by the pressure drop in the Poiseuille law. Initially, the superhydrophobic  
459 capillaries did not display any slipping behavior, but the hydrodynamic behavior changed  
460 with time with intermediate metastable slipping state (slipping length  $\sim 23 \mu\text{m}$ ).  
461 Electrophoretic separations were difficult to obtain in freshly prepared superhydrophobic  
462 capillaries due to the presence of air bubbles leading to unstable current intensity. After a few  
463 (typically 5) instable runs, electrophoretic separations of peptides display improved separation  
464 efficiencies (by a factor  $\sim 2$ ) compared to fused silica capillaries, demonstrating the possibility  
465 to improve electrophoretic separations by using superhydrophobic coatings. This first proof-  
466 of-concept should be further studied to find better coating long-term stability and to improve  
467 the current intensity stability.

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475

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## FIGURE CAPTIONS

**Figure 1.** Scheme of a droplet in the non-wetting Cassie state (A), with the presence of air bubbles beneath the droplet, in the surface anfractuositities, and in the wetting Wenzel state (B), with the droplet filling all the anfractuositities of the surface beneath it.

**Figure 2.** Picture of a ~20  $\mu\text{L}$  droplet (20 mM HEPES, pH 7.45) deposited on a Glaco<sup>TM</sup> coated glass blade (76  $\times$  26 mm) surface. Contact angle, CA = 159°.

**Figure 3.** Ellipsometric scans of Glaco<sup>TM</sup> coated glass blade at the solid-air interface (A) and solid-liquid interface (B). Ultrapure water was used for (B).

**Figure 4.** (A) Tapping mode AFM scan of a Glaco<sup>TM</sup> coated glass blade surface with a bare glass space (black) ; (B) corresponding texture profile of AFM scan showing the size and structure of the Glaco<sup>TM</sup> nanoparticles and clusters ; and (C) zoom in of the Glaco<sup>TM</sup> coating.

**Figure 5.** SEM pictures of Glaco<sup>TM</sup> coated surfaces. Glaco<sup>TM</sup> coated glass blade (A). Beveled capillary end (100  $\mu\text{m}$  internal diameter capillary) (B). (C) and (D) display different zooms of a 100  $\mu\text{m}$  internal diameter capillary inner wall coated by Glaco<sup>TM</sup>. (E) and (F) show different zooms of a 180  $\mu\text{m}$  internal diameter capillary inner wall coated by Glaco<sup>TM</sup>.

**Figure 6.** Visualization of the meniscus in bare silica (A: 100  $\mu\text{m}$  ID) and in Glaco<sup>TM</sup> coated capillaries of different internal diameters (B: 50  $\mu\text{m}$ ; C: 100  $\mu\text{m}$  and D: 180  $\mu\text{m}$  ID) by optical microscopy (magnification x50). Capillaries are filled with blue colored water (dyed with E133 at 1 g/L) and air. Glaco<sup>TM</sup> coated capillaries are prepared according to the protocol given in section 2.2 (see also Table 1).

599 **Figure 7.** DMF fronts obtained at different applied pressures on Glaco™ coated capillary (A):  
600 2 psi (black), 1.5 psi (blue), 1.2 psi (green), 1 psi (orange), 0.8 psi (yellow) and 0.5 psi (red)  
601 and the Poiseuille profiles obtained for different 180 µm ID capillaries (B): bare silica  
602 capillary (Blue ●), Glaco™ coated capillary week #1 (Yellow ▲), week #2 (Red ■), and  
603 week #3 (Green ◆). Glaco™ coated capillaries # 1, 2 and 3 correspond to the same capillary  
604 used in the first week, second week and third week of experiments. Each flow rate  
605 determination was realized in triplicate (error bars are +/- one SD). Experimental conditions:  
606 capillary dimensions 180 µm ID x 40 cm length (30 cm to the detector). BGE: 20 mM HEPES  
607 + 10 mM NaOH at pH 7.65. Marked BGE contains 0.5 % v/v DMF in the HEPES/Na BGE.  
608 BGE flush between runs: 1 psi (~ 70 mbar), 2 min. (C<sub>1</sub>) and (C<sub>2</sub>) show schemes of an air  
609 bubble in the capillary, during week #1 and week #2.

610 **Figure 8.** Electrophoregrams (blue traces) of a peptide mixture obtained on bare silica  
611 capillary (A), freshly prepared Glaco™ coated capillary (B), Glaco™ coated capillary after 5  
612 runs (C), Glaco™ coated capillary after 10 runs (D), and Glaco™ coated capillary after 15  
613 runs (E). Corresponding current intensity are displayed in brown. Inserts show the water  
614 (dyed with E133 at 1 g/L) – air (translucent brown) interface of each capillary. Experimental  
615 conditions: capillary dimensions 100 µm x 40 cm length (30 cm to the detector). Background  
616 electrolyte: Tris / Phosphate 6.5 mM/14.1 mM at pH 2.5. Voltage: 10 kV. Pressure: + 3 psi at  
617 both ends. Injection: 2 psi, 0.2 s. Sample identification: Bursin (1), Lys-His-Gly (2),  
618 Creatinine (3), Ala-Ala (4), Ala-Ala-Ala (5) and Ala-Ala-Ala-Ala (6).

619 **Figure 9.** Separation efficiencies for each peptide obtained on bare silica capillary and on  
620 three different Glaco™ coated capillaries. Plate numbers are average values (+/- one SD)  
621 obtained on 4 successive runs determined from run 5 (the first run with stable current  
622 intensity) to run 9 for each Glaco™ coated capillary. Experimental conditions as in Figure 8.