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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 (GlacoTM), based on simple capillary flushes and thermal
17 stabilization. In this protocol, the control of the air flushing after the introduction of the
18 GlacoTM 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.

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 μm deep x 300 μm wide x 8 cm long) coated by
59 octadecyltrichlorosilane (OTS), give a CA of 120° and 0.92 μm 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 μm
62 thick) and then filled with steel balls of 4.6 mm diameter, giving a CA higher than 150° and
63 47-117 μm slip length [14]. Cylindrical microchannels (150 μm diameter) were prepared with
64 negative print of lotus leaf surface in polystyrene, giving a CA of 160° [15]. Microchannels
65 were coated with carbon nanotubes, giving a CA of 165° and 20 μm 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° , less than 1 μm 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 μm [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° instead of 106° 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 GlacoTM 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. GlacoTM 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 GlacoTM solution, followed by heating at 200°C for 30 min
102 [33]. This process was generally repeated 3-4 times [33]. **Atomic Force Microscopy (AFM)**

103 studies of the GlacoTM 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 GlacoTM 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 GlacoTM deposition for electrophoretic separations.

109

110 **2. Experimental section**

111 **2.1. Chemicals and samples**

112 Glaco Mirror Coat ZeroTM 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 GlacoTM 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. GlacoTM coating**

128 Glass blades (76 x 26 mm, Thermo Scientific, Germany) were coated with GlacoTM by
129 pouring GlacoTM 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 cm²). 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 PlusTM 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 GlacoTM nanoparticles size was measured with a LitesizerTM 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°. GlacoTM 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 GlacoTM 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 GlacoTM 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 m^3/s) at a given pressure ΔP (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 ΔP) was systematically plotted. The slope a of the Q vs ΔP
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 η 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 μ 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 μ 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 μ m, 10 psi 5 min
242 for I.D. 50 μ m, and 1 psi 2 min for I.D. 180 μ 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 δ 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 μ 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™ layer and of the air layer
262 between the immersed Glaco™ 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 (Δ) as a function of the incident angle (φ) for a bare and a
266 Glaco™ coated glass surfaces exposed to air. Around the Brewster angle ($\varphi_{Br}=\arctan(1/n_{Glass}=56.8)$), $\tan\Psi$ and Δ 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™ coating, $\tan\Psi$ and Δ deviate strongly from the ones of the bare surface, which allows
269 us to evaluate the average thickness and refractive of the coating: $n_{Glaco}=1.58\pm 0.1$ and
270 $d_{Glaco}=270\pm 5$ 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™ 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™ surface. The interfacial layer between water and the Glaco™ 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 (ε) 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 γ 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:

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

312 where ΔP 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 ΔP 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 ΔP 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 μm , respectively. Ca numbers are 5.9×10^{-3} ,
318 2.3×10^{-3} , 7.6×10^{-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 μm 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 μm 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 μm 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 μm which is very close to the expected value of 90 μm , assuming no-slip boundary
356 conditions at the silica surface. As for the superhydrophobic 180 μm 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 μm I.D. capillary generate a pressure drop ΔP_{bubble} of ~ 100 Pa taking γ
 361 $= 72$ N/m, $R_c = 90$ μm , $\theta_r = 145^\circ$ 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 GlacoTM 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 μm , 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 GlacoTM 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° and 45°
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 μm and 50 μm 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 μm 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 γ the superficial tension of the BGE (72×10^{-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 μm and 180 μm . The
451 pressure of the air flush to remove the GlacoTM 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 μm 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 ~ 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 μL droplet (20 mM HEPES, pH 7.45) deposited on a GlacoTM coated glass blade (76 \times 26 mm) surface. Contact angle, CA = 159°.

Figure 3. Ellipsometric scans of GlacoTM 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 GlacoTM coated glass blade surface with a bare glass space (black) ; (B) corresponding texture profile of AFM scan showing the size and structure of the GlacoTM nanoparticles and clusters ; and (C) zoom in of the GlacoTM coating.

Figure 5. SEM pictures of GlacoTM coated surfaces. GlacoTM coated glass blade (A). Beveled capillary end (100 μm internal diameter capillary) (B). (C) and (D) display different zooms of a 100 μm internal diameter capillary inner wall coated by GlacoTM. (E) and (F) show different zooms of a 180 μm internal diameter capillary inner wall coated by GlacoTM.

Figure 6. Visualization of the meniscus in bare silica (A: 100 μm ID) and in GlacoTM coated capillaries of different internal diameters (B: 50 μm ; C: 100 μm and D: 180 μm ID) by optical microscopy (magnification x50). Capillaries are filled with blue colored water (dyed with E133 at 1 g/L) and air. GlacoTM 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. (C₁) and (C₂) 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.