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1 Light-Induced Crystallization-Driven Formation of Hierarchically
2 Ordered Superhydrophobic Sol-Gel Coatings

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20

21 **Abstract**

22 Nano/micro structures are crucial for superhydrophobic surfaces, but rare are methods able to
23 generate such dual structuring in a single step using a single precursor. We show that the
24 visible light-controlled self-assembly of bis-silylated alkane precursors can create in one-step
25 organosilica coatings exhibiting two levels of hierarchy: lamellae at nanoscale, and plate-like
26 crystals at microscale. Crystallization rate can be precisely controlled by alkylene bridging
27 group and irradiance. This allowed us to achieve superhydrophobic properties by the creation
28 of a dense and uniform network of nanostructured microcrystals with high surface roughness.
29 The obtained coatings displayed chemical stability, good thermal resistance and high
30 mechanical strength through the cross-linked siloxane structure, which is essential for
31 applications.

32

33 **Keywords:** superhydrophobic; silsesquioxane; photo sol-gel; crystallization

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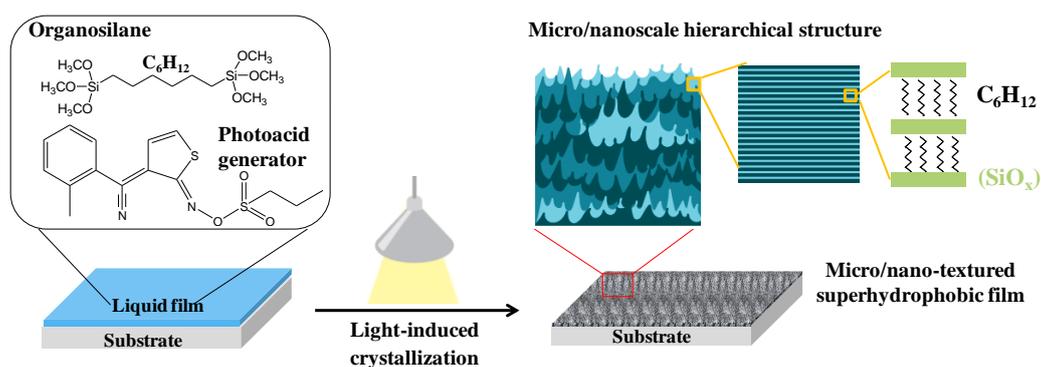
35 **Introduction**

36 Superhydrophobic surfaces combining water contact angles higher than 150° and low
37 contact angle hysteresis have attracted extensive interest from both an economic and an
38 academic perspective [1-3]. High water repellency properties can ensure further developments
39 in many advanced materials with broad potential application [1, 4], such as self-cleaning
40 surfaces [5-7], anti-corrosive coatings [8-11], drag reduction [12-14], or microfluidic devices [15].
41 It is now well established that a combination of low-surface-energy material and hierarchical
42 micro/nanoscale structure is a key feature to fabricate superhydrophobic surfaces [16, 17].

43 Inspired by lotus leaf [18], many different approaches have been developed to achieve both
44 properties in a single coating. Lithography [19], plasma or chemical etching [20], controlled
45 crystallization [21, 22], phase separation phenomena [23], electrochemical deposition [24],
46 chemical vapor deposition [25], and self-assembly [26-28] are the main ones. Despite the
47 diversity of synthetic methodologies, there are still many obstacles to a widespread use of
48 superhydrophobic materials, including multiple steps, use of aggressive chemical reagents, or
49 complex instrumentations [29]. In this context, a facile, cost-effective and environmentally
50 friendly method to superhydrophobic coatings would be highly desirable [6].

51 In response to this major challenge, we report herein a superhydrophobic sol-gel coating
52 produced in a single-step from a single precursor. As depicted in **Figure 1**, the photoinduced
53 condensation of a α,ω -bis-silylated alkane was able to create a superhydrophobic hierarchical
54 structure driven by the self-assembly of the organosilica network. Conventional sol-gel
55 process based on specific organosilane [30-33] or polyhedral oligomeric silsesquioxane [34,
56 35] precursors have long been recognized as a major method for the preparation of
57 superhydrophobic coatings. By contrast, the development of a radiation-mediated sol-gel
58 process has received little attention so far. This in spite of the fact that photopolymerization is
59 considered today as one of the most eco-efficient organic coating technologies [36]. The few
60 studies reporting a light-driven route to superhydrophobic coatings involved volatile organic
61 solvents either to ensure deposition [37, 38] or to induce roughness by phase separation [39]
62 or simple evaporation [40]. In addition, their green credentials were undermined by the use of
63 ultraviolet (UV) radiation and perfluorinated chemicals, both having potential health effects.
64 By contrast, our methodology is based on a solvent-free sol-gel photopolymerization of

65 1,6-bis(trimethoxysilyl)hexane ((H₃CO)₃Si-(CH₂)₆-Si(OCH₃)₃, BC₆TMS) performed at
 66 ambient temperature, low irradiance (< 1 mW cm⁻²) and using a 405 nm light-emitting diode
 67 (LED). A visible radiation promotes a safer environment, while the use of LEDs offer many
 68 technical advantages compared to conventional mercury arcs [41]. While alkoxy silane sol-gel
 69 photopolymerization is already a well established approach to design nanostructured
 70 organosilica coatings [42, 43], it has been harnessed as a way to create a hierarchically
 71 ordered micro/nanostructure which is ideal for achieving superhydrophobicity. By precise
 72 energetic dosage of irradiation, crystallization conditions can be finely tuned to yield in a
 73 single-step a silsesquioxane coating ((OH)_{3-x}O_xSi-(CH₂)₆-SiO_x(OH)_{3-x}, BC₆SQ) composed of
 74 crystalline *nanolayers* assembling in *microcrystals* with high surface roughness. In this work,
 75 the conditions to create a superhydrophobic surface from such hierarchically ordered structure
 76 have been investigated. The challenge lies in the capacity to control template-free
 77 organosilane self-assembly, microcrystals growth and surface energy of the hybrid coating.



78

79 **Figure 1.** Schematic illustration showing the visible light-induced crystallization process of a
 80 bis-silylated alkane precursor forming a micro/nano structured organosilicate coating.

81

82

83 **Experimental section**

84 *Chemicals*

85 1,2-Bis(trimethoxysilyl)ethane (95 %) and 1,6-bis(trimethoxysilyl)hexane (95 %) were
86 supplied by Gelest. Trimethylsiloxy terminated poly(dimethyl siloxane) (PDMS, 3.0 cSt, 550
87 g/mol) was purchased from Fluochem. Trimethoxysilane and 1,9-decadiene were purchased
88 from Aladdin and TCI chemicals (Shanghai), respectively. Photoacid generator Irgacure
89 PAG103 was provided by BASF. All of the chemicals were used as received.

90 *Synthesis of 1,10-bis(trimethoxysilyl)decane*

91 1,10-Bis(trimethoxysilyl)decane was prepared according to the previous literature procedure
92 [44]. Typically, 6.9 g of 1,9-decadiene (0.05 mol), 12.3g of trimethoxysilane (0.1 mol) and 0.35
93 ml of chloroplatinic acid in isopropanol (2.73×10^{-3} M) were mixed together by magnetic
94 stirring, then the mixture was heated to 100 °C and refluxed for 6 hours under nitrogen
95 atmosphere. After distillation of the reaction mixture under vacuum, 6.7 g (35 % yield) of
96 1,10-bis(trimethoxysilyl)decane was collected. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 0.58 (t, 4
97 H), 1.17–1.6 (m, 34 H), 3.7 (q, 12 H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 10.3, 18.3, 22.7,
98 29.2, 29.5, 33.2, 58.2.

99 *Preparation of hierarchically ordered coating*

100 In a typical procedure, photoacid generator (PAG103, 0.5 % wt.) was dissolved in a mixture
101 of 1,6-bis(trimethoxysilyl)hexane and PDMS (75/25 wt. %) to form a photolabile solution in
102 the absence of light. Then the resultant formulation was deposited on a silicon wafer or glass
103 substrate by spin coating (1000 rpm, 20 s) to produce a liquid coating. UV-curing was
104 performed at room temperature under the light of a LED lamp (Shenzhen xianghe, 20 W) with

105 a controlled irradiance from 20 to 0.1 mW cm⁻². The samples were irradiated 1800 s to yield
106 solid silsesquioxane hybrid coatings (~ 4 μm). During irradiation, the relative humidity (RH)
107 was maintained between 50 and 55 %.

108 *Characterization*

109 Infrared spectra were recorded with a spectrophotometer equipped with a MCT detector. The
110 resolution of the infrared spectra was 2 cm⁻¹. X-ray diffraction patterns (XRD) were obtained
111 on a Bruker D8-Discover diffractometer with fixed slits using Cu/Kα radiation ($\lambda = 1.5418 \text{ \AA}$)
112 and θ - 2θ mounting. Before analysis, coatings on silicon wafers were directly deposited on a
113 plastic sample holder. Data were collected between 1 and 30 ° 2θ degrees (XRD) with a
114 scanning step of 0.01° s⁻¹. Morphologies of the samples were characterized by scanning
115 electron microscopy (SEM, Hitachi S3000N microscope working at 30 kV). The samples being
116 non-conductive, they were metalized with gold (15 nm thickness). Water contact angles were
117 measured by sessile drop experiments on a DSA25 contact angle goniometer (Krüss GmbH,
118 Germany) with 6 μL deionized water droplet. Atomic Force Microscopy (AFM) measurements
119 were carried out in a Bruker Multimode IV, with a Nanoscope V controller and an E “vertical”
120 scanner, by the Peak Force Quantitative Nanomechanical Mapping (PF-QNM, Bruker) method.
121 PF-QNM is a contact AFM mode, based on the force-volume method. In this method, force
122 distance curves are collected by nanoindentation of the sample in a point-by-point mode.
123 During measurement, the maximum (peak force) is controlled at each pixel to obtain
124 force-distance curves which are then used as feedback signal. In this method, the loading and
125 unloading force-distance curves are collected at a frequency of 2 kHz at each position within
126 the mapped area of the specimen. In parallel to topography images, information on material

127 elasticity (Young's modulus), tip-to-surface adhesion were obtained. All the experiments were
128 carried out in air and at room temperature. $5\ \mu\text{m} \times 5\ \mu\text{m}$ (256×256 pixels at 0.5 Hz) were taken
129 at three different areas on the sample surface. To get relevant results, the cantilever and the tip
130 geometry are taking into account in the PF-QNM measurements. Thus, a calibration procedure
131 was first followed. All quantitative measurements were carried out with RTESPA-300
132 cantilever (Bruker, USA) with a spring constant of $40\ \text{N m}^{-1}$ and resonance frequency of 300
133 kHz, a width of $40\ \mu\text{m}$ and a length of $125\ \mu\text{m}$. Thanks to the Sader method [45] (using the
134 length, the width, the resonance frequency and the quality factor of the cantilever) the actual
135 spring constant was determined and found to be around $42\ \text{N m}^{-1}$. Then, the deflection
136 sensitivity (around $33\ \text{nm V}^{-1}$) was measured on a sapphire surface. Tip radius was calibrated
137 against a polystyrene standard provided by Bruker. The measured value of the tip radius was 30
138 nm. The Poisson's ratio was assumed to be equal to 0.3. For all experiments, samples were
139 previously (at least half a day before) fixed on a sample holder with a double-sided tape. X-ray
140 photoelectron spectroscopy (XPS) analyses were performed with a VG Scienta SES 2002
141 spectrometer equipped with a monochromatized $\text{Al(K}\alpha\text{)}$ X-ray source (1486.6 eV), a
142 hemispherical analyzer and an electron gun to compensate the charging effect. The high
143 resolution spectra and wide scan were recorded with pass energy of 100 eV and 500 eV
144 respectively. The analyzed zone had a surface of $24\ \text{mm}^2$. The decomposition of the spectra into
145 different components was performed with Gaussian-Lorentzian, after having subtracted a
146 Shirley-type background. The mean composition of the sample surface expressed in atomic
147 percentages was determined using integrated peak areas of each component, and taking into
148 account the transmission factor of the spectrometer, means free path, and sensibility factors of

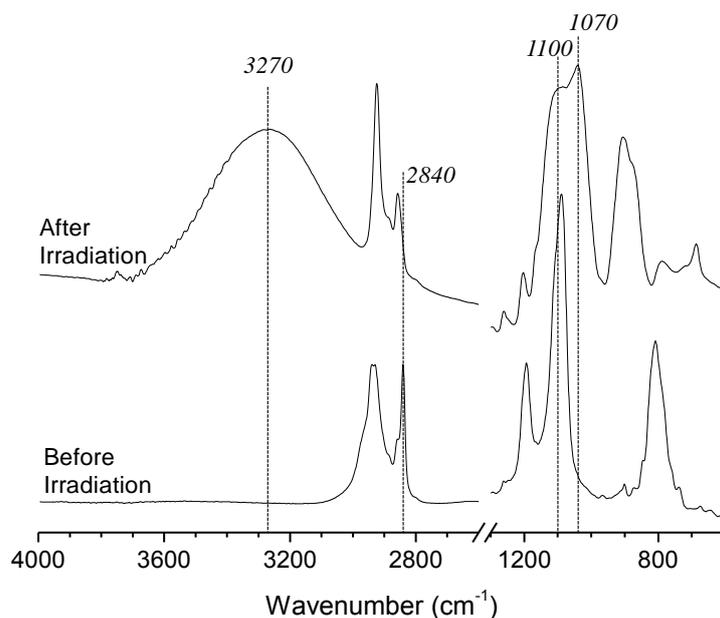
149 each atom. The bouncing of the droplets was recorded with a high-speed camera (4M180-CL
150 from IO Industries Inc., London, ON, Canada) at a frame rate of 500 fps. The impact velocities
151 were calculated from the five last images before the contact between the droplet and the surface.
152 We used a microsyringe with a tip geometry allowing to deliver water droplets with a diameter
153 of $2.7 \text{ mm} \pm 0.2 \text{ mm}$. The height of the syringe tip was increased in order to reach high impact
154 velocities. With these droplet diameters, the highest impact velocities considered in this work
155 were around than $1.2 \text{ m/s}^{-1} \pm 0.1 \text{ m}\cdot\text{s}^{-1}$. Beyond these velocities, fragmentation of the droplets
156 was observed. As for the sessile drop experiments, we used fresh deionized water. The abrasion
157 resistance of the superhydrophobic surface was evaluated by a homemade Taber abrasion
158 equipment. The test specimen was placed on the abrasion tester. A 100 g load was then placed
159 on top of the abrader wheel (1500-mesh sandpaper) and allowed to spin for a specified number
160 of revolutions at a speed of $3 \text{ cm}\cdot\text{s}^{-1}$. The contact area between the abrader wheel and the
161 underlying superhydrophobic coating was 4.8 cm^2 . Water CA and sliding angle of test
162 specimen were measured after different number of abrasion cycles.

163

164 **Results and discussion**

165 The synthesis of bridged silsesquioxane coating BC₆SQ proceeds through an
166 acid-catalyzed sol-gel photopolymerization in presence of a commercial photoacid generator
167 (PAG, (5-propylsulfonyl-oxyimino-5H-thio-phen-2-ylidene)-(2-methylphenyl) acetonitrile). Upon
168 exposure to visible light, *n*-propyl sulfonic acid is liberated, acting as a catalyst for
169 hydrolyzing methoxysilyl (Si-OCH₃) functions into Si-OH, and for their subsequent
170 condensation into siloxane (Si-O-Si) bonds. This series of reactions was triggered by

171 irradiating a BC₆TMS/PAG coating (1/0.005 wt%, thickness: 4 μm) with a 405 nm LED lamp at
172 low irradiance (0.5 mW cm⁻²) during 30 min. The efficiency of the photo sol-gel process was
173 supported by FTIR spectroscopy (**Figure 2**) through the disappearance of the CH₃ symmetric
174 stretch of SiO-CH₃ groups at 2840 cm⁻¹ and the concomitant emergence of a broad band at
175 3000-3400 cm⁻¹, indicative of the silanol formation. The presence of asymmetric stretching
176 bands of siloxane bonds at 1100 and 1070 cm⁻¹ proved the formation of the
177 polysilsesquioxane network. It was further evidenced by ²⁹Si SPE-MAS NMR spectroscopy
178 (see spectrum in Figure S1 in supporting information) which revealed T¹ (-49 ppm,
179 C-Si(OR)₂(O-Si), 15.9 %), T² (-58 ppm, C-Si(OR) (O-Si)₂, 59.4 %) and T³ (-68 ppm,
180 C-Si(O-Si)₃, 24.7 %) siloxane species.



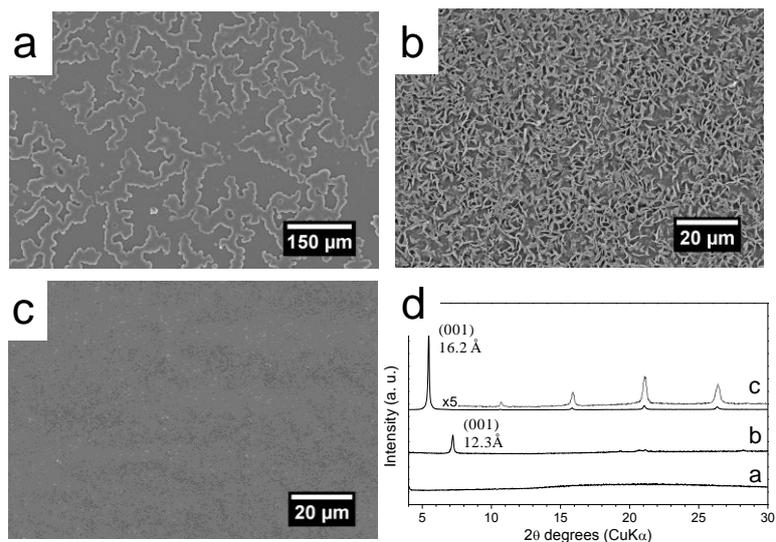
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182 **Figure 2.** FTIR spectra of BC₆TMS-derived coating before and after the sol-gel
183 photopolymerization (I = 0.5 mW cm⁻², RH = 50 %, T = 25 °C).

184

185 Scanning electronic microscopy (SEM) was used to assess the possible surface

186 microstructuration. **Figure 3** displays a representative image for BC₆SQ as well as two other
187 images obtained with bridged precursors exhibiting other chain lengths
188 ((CH₃O)₃SiC_nH_{2n}Si(OCH₃)₃, n = 2 and 10). BC₂SQ (**Figure 3a**) containing the shortest
189 bridging group formed a surface locally uneven and rough, resulting only in a moderate water
190 contact angle (CA) of 78.0° ± 0.9°. Upon increasing the chain length, BC₆SQ (**Figure 3b**)
191 revealed a uniform, highly rough surface, driving a much higher CA (129.5° ± 1.1°). In contrast,
192 BC₁₀SQ (**Figure 3c**) exhibited only local features protruding from the plane, leading to a sharp
193 decrease of CA (85.5° ± 0.9°). Further investigation of the hybrid coatings' nanostructure was
194 performed by X-ray diffraction (XRD). As shown in **Figure 3d**, the coating derived from the
195 ethylene precursor (trace **a**) was mainly amorphous. In contrast, increasing the alkylene chain
196 length to C₆ (trace **b**) led to a single sharp diffraction signal, indicative of a long range ordered
197 sample. The onset of a highly ordered nanostructure was even more evident with the BC₁₀SQ
198 coating whose XRD pattern (trace **c**) displayed 5 reflection peaks from (001) to (005)
199 suggestive of a lamellar mesostructure. In the latter two cases, the (001) peaks at 12.3 Å (**b**) and
200 16.2 Å (**c**) were consistent with an interlamellar distance for structures based on alternating
201 stacks of C_nH_{2n} bridging groups connected to a single siloxy chain. As expected in organosilane
202 self-assembly, a higher ordering is driven by longer alkylene bridging groups because of
203 stronger Van der Waals interactions [46].

204



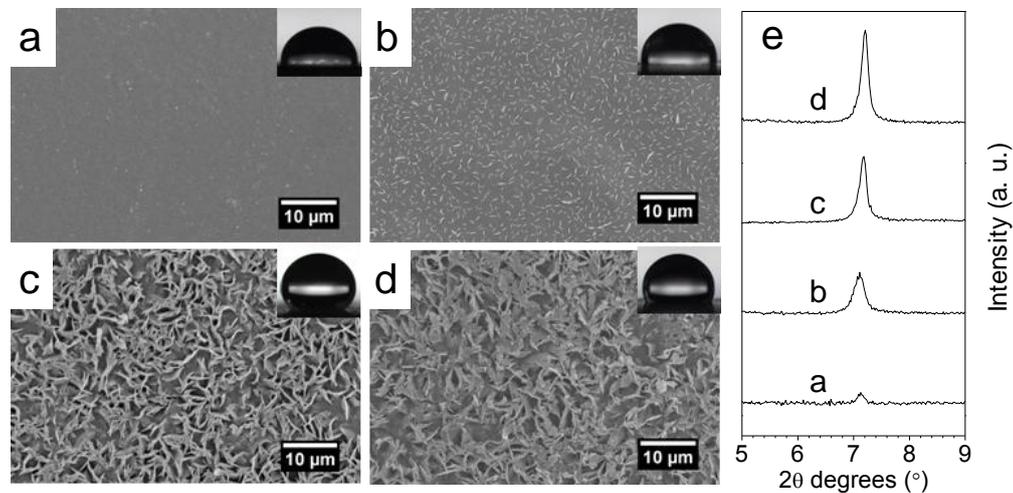
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206 **Figure 3.** SEM micrographs of BC_nSQ samples derived from BC_nTMS precursors
 207 $[(CH_3O)_3SiC_nH_{2n}Si(OCH_3)_3]$, $n = 2$ (a), 6 (b), 10 (c)]. XRD patterns of the three
 208 photopolymerized BC_nSQ hybrid coatings (d). $I = 0.5 \text{ mW cm}^{-2}$, 30 min irradiation.

209

210 In addition, the microstructures observed by SEM may be assigned to polycrystals formed
 211 by the assembly of dense and regular arrays of nanolamellae. This assumption is supported by
 212 images of polarized optical microscopy confirming that the three samples (Figure S2) exhibit
 213 birefringence (anisotropy of refraction) that is characteristic of their crystalline structure.
 214 Although the microcrystals stem from the growth of lamellar nanocrystals, their density and
 215 uniformity were strongly dependent on the chain length. Compared to other precursors,
 216 BC_6SQ was unique for its ability to form a homogeneous hierarchical surface through a
 217 crystallization process expressing at both nano- and microscale levels. Consequently, in the
 218 view to provide superhydrophobic properties, C_6TMS was preferentially used in the rest of
 219 this study. Next efforts were focused on utilization of light, in particular irradiance, to
 220 precisely control the morphology of the BC_6SQ surface. The objective was to optimize

221 crystallization conditions in a way to create hierarchically ordered coating displaying a
222 uniform and highly rough spiky surface.



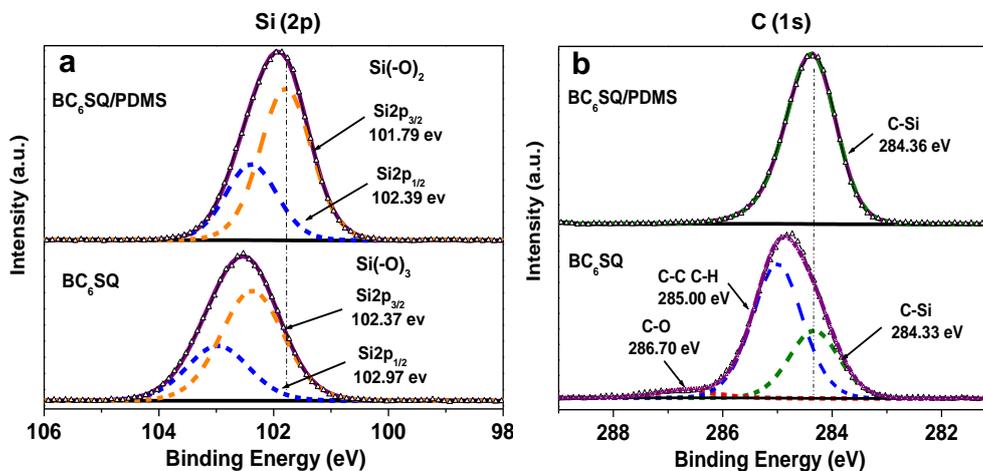
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224 **Figure 4.** SEM micrographs of BC₆SQ prepared at different irradiances: 20 (a), 2 (b), 0.5 (c),
225 0.1 (d) (unit: mW cm⁻², 30 min irradiation). The corresponding (001) XRD peak of each
226 sample is shown on the right side (e).

227

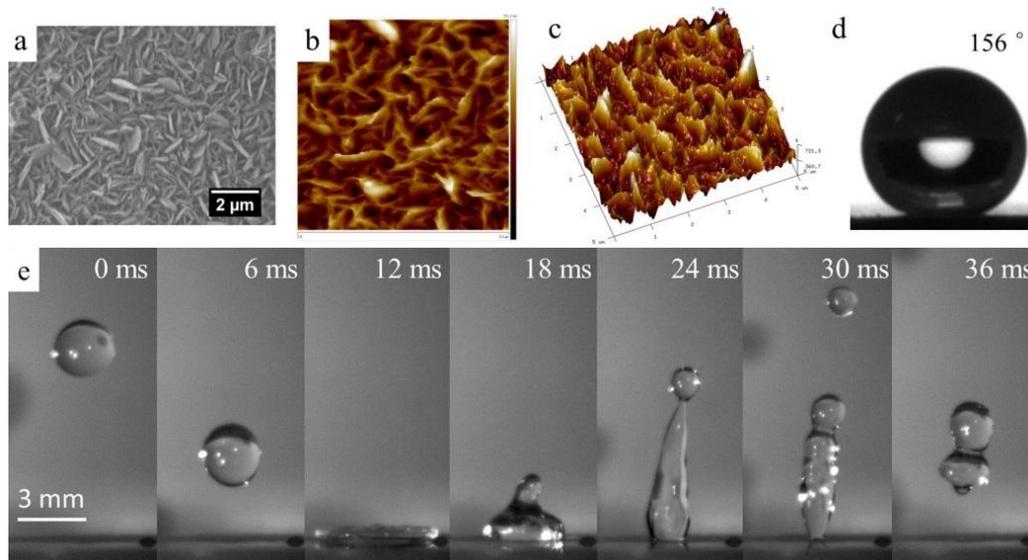
228 Both nano- and microstructures are expected to be influenced by the crystallization time,
229 which is dependent on the condensation rate [47-48]. One key advantage of a
230 radiation-mediated process is that a modulation of irradiance represents an efficient means to
231 control this condensation kinetics. **Figure 4a-d** show SEM images of BC₆SQ prepared at
232 different irradiances (0.1 - 20 mW cm⁻²). A smooth surface with limited hydrophobic
233 properties was obtained (**Figure 4a**, CA = 82.0° ± 0.7°) at 20 mW cm⁻². In accordance with
234 this result, the corresponding XRD pattern (**Figure 4e**) featured only a low intense (001) peak
235 because condensation reactions were presumably too fast to favor self-assembly. Upon
236 decreasing irradiance to 2 mW cm⁻², microcrystals appeared at the coating surface, resulting
237 in an increased hydrophobicity (**Figure 4b**, CA = 95.0 ° ± 0.9°). Consistently, there was a

238 sharpening and intensity increase of the (001) reflections, suggesting a higher level of
 239 ordering (**Figure 4e**). At 0.5 mW cm^{-2} , the level of ordering still increased, which translated in
 240 sharper reflection peaks. Concomitantly, the size and number of flat and edgy plates on the
 241 coating surface increased, resulting in a larger CA value (**Figure 4c**, $\text{CA} = 129.5^\circ \pm 1.1^\circ$). At
 242 0.1 mW cm^{-2} , the XRD pattern followed the same trend, but the water contact angle fell
 243 markedly (**Figure 4d**, $\text{CA} = 112.0^\circ \pm 1.2^\circ$), likely as a result of the collapse of the poorly
 244 condensed microstructure. Therefore, an irradiance 0.5 mW cm^{-2} (**Figure 4c**) seemed the best
 245 trade-off. Under these conditions, crystallization time was slow enough to drive a high level
 246 of organization, which proved to be beneficial for a higher crystallinity and the emergence of
 247 well-defined nano- and micro-structures. Slow condensation is assumed to increase the
 248 nucleation rate and the density of flakes at the surface contributing to increase roughness. In
 249 these conditions, the inhomogeneity and size of the pores increase, contributing to the
 250 increase of water CA. Nevertheless, the present system was not yet able to achieve
 251 superhydrophobic properties. One possible reason is a too high surface energy of the bridged
 252 silsesquioxane structure.



253
 254 **Figure 5.** Si (2p) (a) and C (1s) (b) core level XPS spectra of BC₆SQ and BC₆SQ/PDMS.

255 In order to increase the water CA, a small amount of trimethylsilyl terminated
256 poly(dimethylsiloxane) (PDMS, 550 g/mol) was added. The goal was to coat the BC₆PSQ
257 microstructure with a material having a lower surface energy than alkyl bridged
258 silsesquioxane while keeping the advantage of a one-step procedure. The analysis of the XRD
259 pattern confirmed that this additive did not significantly alter the nanoscale organization
260 (Figure S3), with only a slight broadening of the XRD signal. In order to assess the surface
261 migration ability of PDMS chains, X-ray photoelectron spectroscopy (XPS) was performed
262 with BC₆SQ/PDMS and pure BC₆SQ (**Figure 5**). In both cases, the Si2p peak (**Figure 5a**)
263 displayed two components, Si2p_{3/2} and Si2p_{1/2} with a spin-orbit coupling of 0.6 eV. However,
264 the position of these two features was distinct depending on the sample, suggesting a different
265 Si environment. As expected, the binding energies in BC₆SQ (102.37 eV, 102.97 eV) were in
266 agreement with the presence of T siloxane species RSi(OH)_x(OSi)_{3-x} [49]. By contrast, the
267 positions in BC₆SQ/PDMS, (101.79 eV, 102.39 eV) were consistent with a majority of D
268 siloxane units R₂Si(OSi)₂ [49] and correspond well to literature values for PDMS [50]. As
269 shown in **Figure 5b**, the C1s peak of pure BC₆SQ could be fitted into three peaks assigned at
270 C-O (286.70 eV), C-C and C-H (285.00 eV) and C-Si (284.33 eV). Conversely, the C1s peak
271 of BC₆SQ/PDMS was deconvoluted only in a single peak centered at 284.36 eV assigned to
272 C-Si bonds [50], which is the only C-containing bonds in the PDMS used. Therefore, XPS
273 survey of Si and C areas both supported the formation of a PDMS-rich surface region in
274 BC₆SQ/PDMS.



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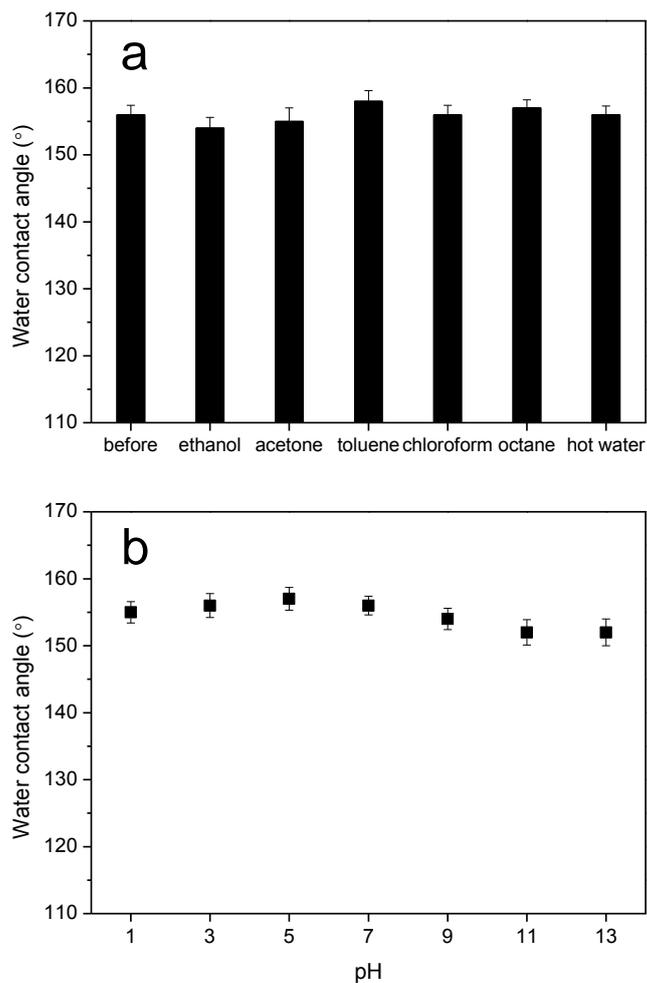
276 **Figure 6.** (a) SEM micrographs of the surface of BC₆SQ/PDMS coating obtained by visible
 277 light induced polymerization (0.5 mW cm⁻², 30 min irradiation). Inset: shape of water droplet
 278 on BC₆PSQ/PDMS coating surface); (b) AFM height image (5 μm × 5 μm); (c) AFM 3D
 279 topography of BC₆PSQ/PDMS coating surface; (d) High-speed images sequence of a water
 280 droplet hitting the BC₆PSQ/PDMS coating at an impact velocity of 1.2 m·s⁻¹ ± 0.1 m·s⁻¹
 281 (falling height of 5 cm).

282

283 In addition, SEM observation (**Figure 6a**) revealed that microcrystals of BC₆SQ/PDMS
 284 still formed a homogeneous array of flat plates exhibiting sharp edges, giving the
 285 microstructure a shape similar to sand rose rocks. AFM characterization (**Figure 6b-c**)
 286 confirmed such morphology presenting a high roughness (arithmetic average roughness $R_a =$
 287 98 ± 10 nm). The crystals were shaped like petals or flat plates, growing up to around 1 μm.
 288 Remarkably, this surface showed high superhydrophobicity. The repellency was such that it
 289 was extremely difficult to measure an equilibrium contact angle or a contact angle hysteresis,
 290 the water droplets just rolling off the surface. While scanning the surface with the water

291 droplet, it was possible however to find some anchoring points corresponding to local
292 heterogeneities in the coating. In this case, the water droplet contact angle was 156° (**Figure**
293 **6d**). Additionally, the CA hysteresis was found to be zero, as expected from a surface on
294 which water droplets could not adhere. The bouncing drop technique was used to further
295 characterize the resistance of the surface texture to wetting. The bouncing of water droplets
296 on BC₆SQ/PDMS surface was observed using a high speed video camera, with increasing
297 falling heights. It was not possible even for the highest falling height (just before
298 fragmentation of the droplet) to produce the forced wetting of the surface texture, the droplet
299 still detaching from the substrate after the first impact, and bouncing on the surface (see
300 **Figure 6e**). Such a water repellency and pressure resistant superhydrophobic surface is
301 remarkable and might be particularly relevant for underwater applications.

302 In order to evaluate the environmental stability and solvent resistance properties of this
303 superhydrophobic surface, the influence of exposure to organic solvents, hot water and
304 aqueous solutions displaying a range of pH was examined (**Figure 7**). Remarkably, the
305 superhydrophobicity of BC₆PSQ/PDMS coating was preserved after immersion during 30
306 min in different solvents: ethanol, acetone, toluene, chloroform, octane or boiling water
307 (**Figure 7a**). In all instances, for droplets adhering locally on some defects, the CAs were still
308 extremely high ($> 150^\circ$), and no contact angle hysteresis could be measured ($\Delta\theta = 0^\circ$). Even
309 after being exposed to air for 3 months, the surface retained its water-repellent property.
310 Furthermore, the superhydrophobicity of BC₆PSQ/PDMS coating was maintained even after
311 24 h immersion in acid/alkali solution with pH from 1 to 13 (**Figure 7b**).

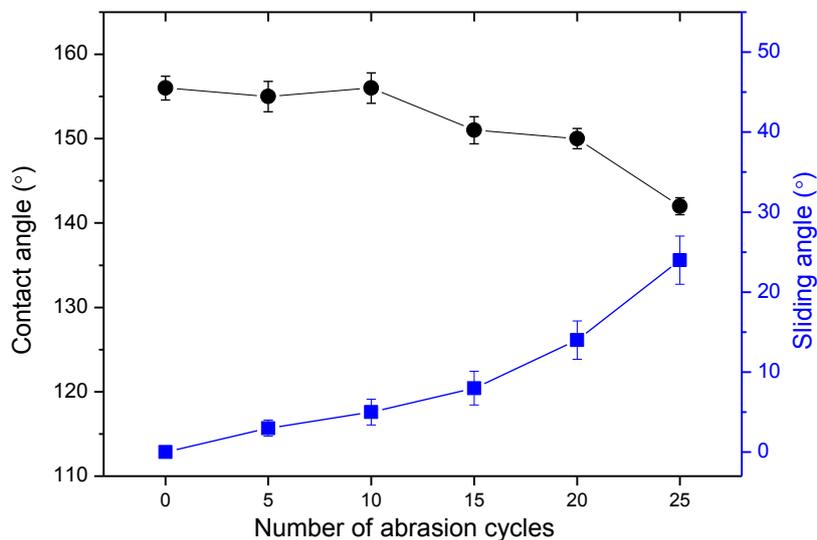


312

313 **Figure 7. (a)** The solvent-resistance of the BC₆PSQ/PDMS superhydrophobic coating upon
 314 treatment with various solvents during 30 min; **(b)** Variation of water CA for BC₆PSQ/PDMS
 315 superhydrophobic coating after immersion in aqueous solutions with different pH values for
 316 24 h.

317 The mechanical durability of the BC₆PSQ/PDMS superhydrophobic coating was also
 318 assessed using an abrasion wear test [51]. The methodology of the abrasion test involved
 319 rubbing the BC₆PSQ/PDMS coating surface against a rotating abrader wheel (see
 320 characterization section for details). The variations of the water CA and sliding angle (SA)
 321 values along with abrasion cycles are shown in **Figure 8**. Interestingly, the surface of
 322 BC₆PSQ/PDMS coating maintained superhydrophobicity ($\geq 150^\circ$) even after 20 abrasion

323 cycles. Although the SA values increased with the number of abrasion cycles, it is only 14 °
324 after 20 cycles of abrasions. Such results indicated the mechanical stability of the hybrid
325 coating surface.

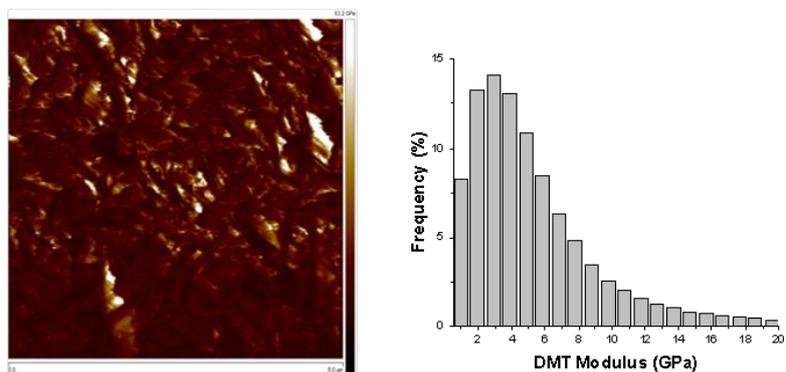


326

327 **Figure 8.** Water CA and sliding angle of the BC₆PSQ/PDMS superhydrophobic coating
328 surface as a function of abrasion cycles with a pressure of ~2.4 kPa.

329

330 Such coating robustness was attributed to siloxane cross-linked structure as well as the
331 high modulus value provided by the crystalline structure. In agreement with these two
332 hypotheses, ²⁹Si solid state NMR spectroscopy (Figure S4) revealed a relatively high degree
333 of condensation (72 %). Additionally, the Derjaguin–Müller–Toporov (DMT) fit model was
334 used to estimate the elastic modulus using the unloading parts of the AFM force curves. The
335 average values of the DMT elastic modulus of BC₆SQ/PDMS surface was 3.2 ± 1.2 GPa
336 **(Figure 9).**



337

338 **Figure 9.** Representative maps DMT modulus and corresponding histogram of the
 339 BC₆SQ/PDMS sample obtained with PeakForce QNM.

340

341 **Conclusion**

342 We have demonstrated a new strategy based on light-induced crystallization to fabrication of
 343 hybrid superhydrophobic coatings for the first time. Of particular interest is that the described
 344 light-induced crystallization process proceeds in bulk without any solvent and water, thus
 345 obviating not only the insolubility problem of precursors but also the environmental issue.
 346 The one-step sol-gel polymerization of bridged precursor BC₆TMS is catalyzed by *in situ*
 347 light irradiation generated photoacid of *n*-propane sulfonic acid that formed
 348 polysilsesquioxane hybrid coating shows micro/nanoscale hierarchical structure.
 349 Template-free organosilane self-assembly accounts for formation of crystalline nanolayers
 350 assembling in flat plates microcrystals. With sufficient roughness simply tuned by irradiation
 351 intensity, the micro/nanotextured surfaces result in high water contact angles ($\geq 156^\circ$) and no
 352 contact angle hysteresis could be measured ($\Delta\theta = 0^\circ$). Furthermore, the cross-linked
 353 silsesquioxane hybrid coatings are mechanically robust (20 cycles abrasion and with a DMT
 354 elastic modulus value of 3.2 ± 1.2 GPa) as well as chemically (various organic solvents,
 355 acid/alkali solution) and thermally resistant (even for boiling water). Thus, the present
 356 strategy has potential applications for superhydrophobic coatings, in particular for large-area,
 357 temperature or even UV light sensitive substrates.

358

359 *Supporting Information.* ^{29}Si solid state SPE-MAS NMR spectra of the visible LED cured
360 BC_6SQ hybrid coatings (Figure S1), polarized optical microscopy images of the BC_nSQ
361 hybrid coatings (Figure S2), XRD patterns of the visible LED cured hybrid coatings (Figure
362 S3), ^{29}Si solid state SPE-MAS NMR spectrum of the visible LED cured $\text{BC}_6\text{SQ}/\text{PDMS}$ hybrid
363 coatings (Figure S4).

364

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494

Electronic Supplementary Information (ESI)

495

Light-Induced Crystallization-Driven Formation of Hierarchically

496

Ordered Superhydrophobic Sol-Gel Coatings

497

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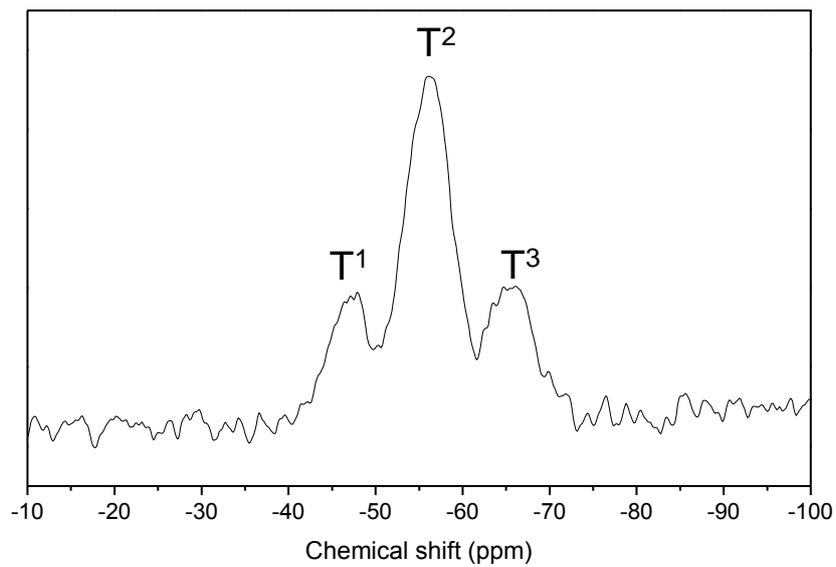
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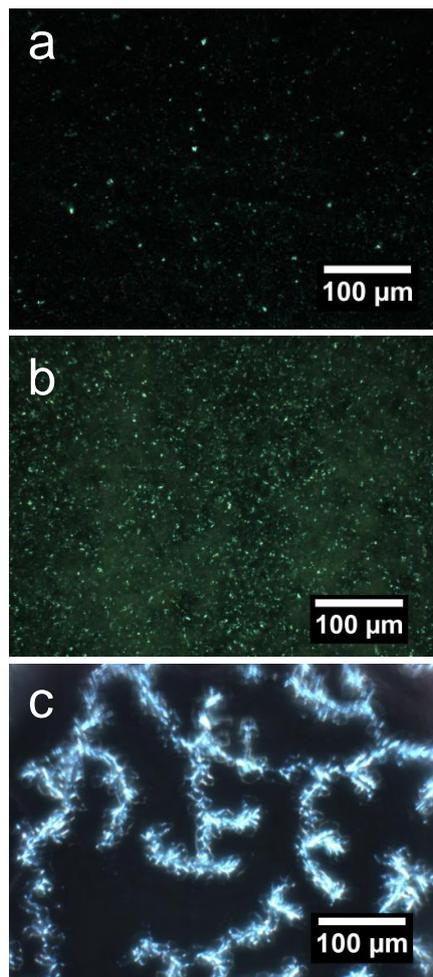
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517 **Figure S1.** ^{29}Si solid state SPE-MAS NMR spectra of the visible LED cured BC_6SQ hybrid

518 coatings derived from BC_6TMS precursor ($I = 0.5 \text{ mW/cm}^2$, $\text{RH} = 50 \%$, $T = 25 \text{ }^\circ\text{C}$).

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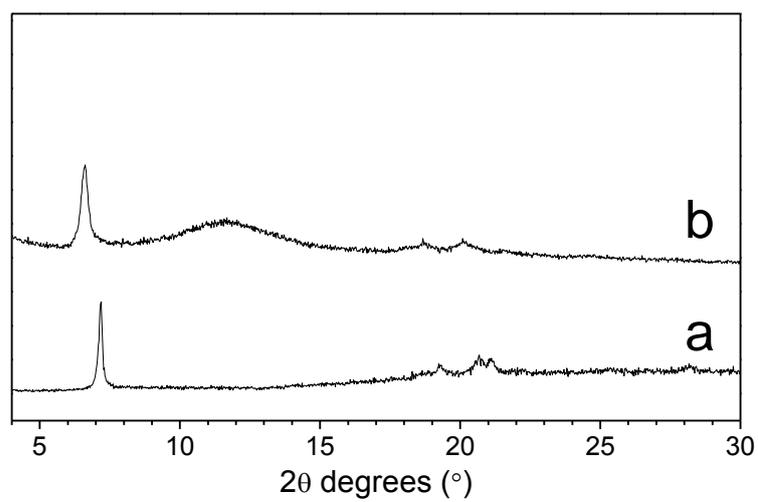


521

522 **Figure S2.** POM micrographs of the BC_nSQ hybrid coatings: (a) BC₁₀SQ, (b) BC₆SQ, and (c)

523 BC₂SQ (I = 0.5 mW/cm², RH = 50 %, T = 25 °C).

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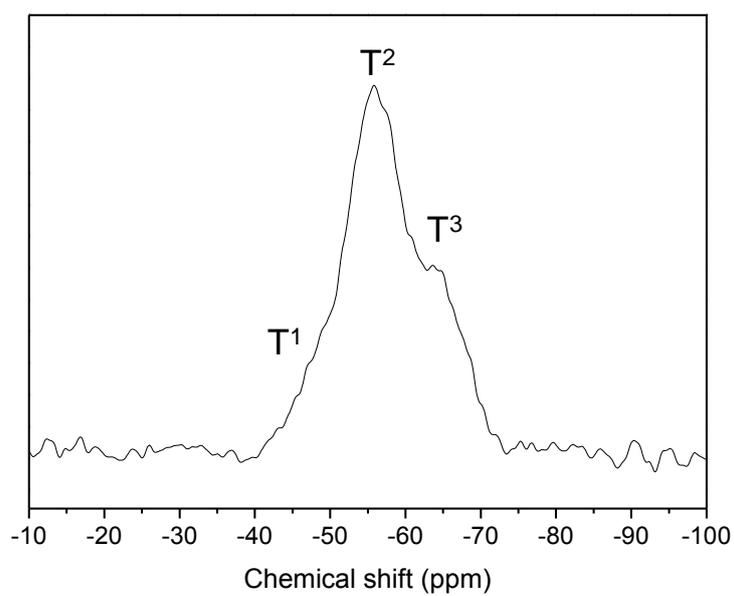


525

526 **Figure S3.** XRD patterns of the visible LED cured hybrid coatings: (a) BC₆SQ; (b)

527 BC₆SQ/PDMS ($I = 0.5 \text{ mW/cm}^2$, RH = 50 %, T = 25 °C).

528



529

530 **Figure S4.** ^{29}Si solid state SPE-MAS NMR spectrum of the visible LED cured $\text{BC}_6\text{SQ/PDMS}$

531 hybrid coatings ($I = 0.5 \text{ mW/cm}^2$, $\text{RH} = 50 \%$, $T = 25 \text{ }^\circ\text{C}$).

532

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534