# Contact Electrochemical Replication of Hydrophilic—Hydrophobic Monolayer Patterns

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onsiderable efforts have been and continue to be devoted in recent years to the advancement of new methods of surface patterning—an issue of obvious central importance for progress in the area of nanofabrication. At present, one is faced with a variety of "unconventional" methods of surface patterning, each of which makes use of a different physical or chemical principle of operation<sup>8</sup> and offers specific advantages for different specific applications. En route to a comprehensive nanofabrication methodology by chemical means (the so-called bottom-up approach), this laboratory has advanced constructive nanolithography (CNL)<sup>2</sup> and constructive microlithography (CML),<sup>3</sup> collectively referred to as constructive lithography (CL), as a generic approach to the nondestructive chemical patterning of highly ordered organosilane monolayers. CL exploits electrochemical transformations that preserve the structural integrity of the patterned monolayer and so allow its direct further utilization as a template in various postpatterning processes of template-guided selfassembly and surface chemical modification.<sup>2-14</sup>

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In CNL, an electrically biased scanning 35 force microscope (SFM) tip bearing a nano-36 droplet of water produced by spontaneous 37 capillary condensation from the ambient is 38 typically used to oxidize terminal  $-CH_3$ 39 40 functions of an OTS/Si monolayer to -COOH<sup>2</sup> (OTS/Si denotes a self-assembled 41 monolayer on silicon derived from the 42 n-octadecyltrichlorosilane, 43 SiCl<sub>3</sub>—(CH<sub>2</sub>)<sub>17</sub>—CH<sub>3</sub>, molecular 44 precursor<sup>2,8,15</sup>). In this manner, planned pat-45 terns of nanometric hydrophilic sites can 46 be inscribed on the highly hydrophobic top 47 surface of an OTS monolayer. In CML, 48 monolayer patterns consisting of hydro-49

ABSTRACT Contact electrochemical replication (CER) is a novel pattern replication methodology advanced in this laboratory that offers the unprecedented capability of direct one-step reproduction of monolayer surface patterns consisting of hydrophilic domains surrounded by a hydrophobic monolayer background (hydrophilic @ hydrophobic monolayer patterns), regardless of how the initial "master" pattern was created. CER is based on the direct electrochemical transfer of information, through aqueous electrolyte bridges acting as an information transfer medium, between two organosilane monolayers self-assembled on smooth silicon wafer surfaces. Upon the application of an appropriate voltage bias between a patterned monolayer/silicon specimen playing the role of "stamp" and a monolayer/silicon specimen playing the role of "target", the hydrophilic features of the stamp are copied onto the hydrophobic surface of the target. It is shown that this electrochemical printing process may be implemented under a variety of experimental configurations conducive to the formation of nanometric electrolyte bridges between stamp and target; however, using plain liquid water for this purpose is, in general, not satisfactory because of the high surface tension, volatility, and incompressibility of water. High-fidelity replication of monolayer patterns with variable size of hydrophilic features was achieved by replacing water with a spongelike hydrogel that is nonvolatile, compressible, and binds specifically to the hydrophilic features of such patterns. Since any copy resulting from the CER process can equally perform as stamp in a subsequent CER step, this methodology offers the rather unique option of multiple parallel reproduction of an initially fabricated master pattern.

**KEYWORDS:** monolayer patterning · AFM · organosilane monolayers · surface wetting · pattern replication · electrochemistry · hydrogels

philic surface regions of micrometric and larger dimensions are analogously created onto a hydrophobic OTS surface using a conductive stamp, which allows the entire desired pattern to be simultaneously printed rather than serially inscribed with a scanning probe.<sup>3</sup>

Both CNL and CML combine methods of surface self-assembly, and particularly organic monolayer self-assembly, with electrochemical oxidation/reduction processes mediated by an interfacial aqueous medium confined to the contact area between a conductive SFM tip or a conductive stamp and a conductive monolayer-coated target surface (typically but not only<sup>4,5</sup> OTS/Si) on which the desired pattern is inscribed (tip)<sup>2,4,5,16</sup> or printed (stamp).<sup>3</sup> As such, CL

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Figure 1. Schematic representation of the CER process: A patterned organosilane monolayer consisting of hydrophilic surface regions (coated with a thin layer of water or of a suitable water absorbing material) surrounded by a hydrophobic, waterfree OTS/Si background (monolayer STAMP, A) is pressed against a hydrophobic OTS/Si monolayer (TARGET monolayer, B) (top left). Upon the application of an appropriate voltage bias between A and B, with B positively biased (top right), the hydrophilic features of the STAMP are reproduced onto the TARGETeo (electrooxidized target). The electrochemically printed replica pattern (B), consisting of hydrophilic OTSeo/Si (electrooxidized OTS) features surrounded by a hydrophobic OTS/Si mono-layer background (OTSeo@OTS), is a mirror image of the monolayer stamp pattern (A) (bottom).

is related, on the one hand, to surface patterning methods such as microcontact printing ( $\mu$ CP),<sup>1,8,17-21</sup> dippen nanolithography (DPN)<sup>22-25</sup> and scanning nearfield photolithography (SNP)<sup>26</sup> and, on the other hand, to local oxidation lithography (LOL).<sup>27-30</sup> In a typical configuration, µCP employs a topographically patterned polymeric stamp to locally deliver a molecular "ink" that forms a self-assembled monolayer on the target surface (typically alkanethiols on gold) in the areas contacted by the protruding features of the stamp.<sup>1</sup> DPN employs an SFM tip as tool for planned delivery of molecular "inks" to preselected sites on the target surface (typically alkanethiols on gold, like in the µCP process).<sup>22,24</sup> SNP uses a scanning near-field optical tip to locally modify appropriate monolayers by photochemical transformations,<sup>26</sup> and LOL is an electrochemical method that operates similarly to CL, the pattern being, however, created by the local oxidation of the target surface itself (e.g., silicon).<sup>27</sup>

CL offers a series of rather unique capabilities compared with other methods of surface patterning, which make it particularly well suited as a platform for bottom-up nanofabrication.<sup>2–14</sup> However, regardless of the specific physical or chemical process utilized in the creation of a particular surface pattern, all known methods of surface patterning are equally plagued by the apparent incompatibility of ultimate miniaturization with speed; in general, fast parallel methods like photolithography or printing (including  $\mu$ CP and CML) do not reach the smallest desired dimensions, whereas methods that may in principle go down to the nanoscale, like the various scanning probe nanolithographies

(including DPN, SNP, LOL, and CNL) are serial 100 techniques and thus too slow for most practi-101 cal purposes. Is this an inherent fundamental 102 limitation or might there be ways to overcome 103 it? Using large arrays of tips working in parallel, 104 DPN strives to reach high throughput and cover 105 centimeter-size surfaces while preserving the 106 serial mode of pattern writing at the level of the 107 individual tip.<sup>25</sup> Here we present a series of ex-108 perimental results that hold promise for the ad-109 vancement of a true parallel approach to this 110 basic problem, building on the recently demon-111 strated new concept of contact electrochemical 112 replication (CER) of hydrophilic @ hydrophobic 113 monolayer patterns<sup>31</sup> (Figure 1). 114

As illustrated in Figure 1, the hydrophilic fea-115 tures of a "monolayer stamp" (A), conveniently 116 produced by the appropriate patterning of a 117 highly hydrophobic OTS/Si monolayer, may be 118 copied electrochemically onto the surface of a 119 pristine OTS/Si "target monolayer"(B) brought in 120 contact with the stamp upon the application of 121 an appropriate voltage bias between stamp and 122 target, provided a thin layer of water or of a suit-123 able water absorbing material is present at the 124

interface between the hydrophilic features of the stamp 125 and the target. In this CER process, the monolayer 126 stamp (A) plays the role of cathode and the target 127 monolayer (B) of anode, in a manner analogous to the 128 electrochemical inscription of nanopatterns with a con-129 ductive SFM tip<sup>27,28,2,4,16</sup> (in CNL) or the printing of mi-130 cropatterns with a conductive metal stamp<sup>3,29,30</sup> (in 131 CML). At the cathode (stamp), electrolysis of water con-132 ceivably results in liberation of hydrogen<sup>5,27</sup> (with pres-133 ervation of the stamp pattern), whereas at the anode, 134 the terminal -CH<sub>3</sub> groups of the target monolayer 135 (OTS) are electrochemically oxidized to -COOH (OT-136 Seo),<sup>2</sup> the OTS  $\rightarrow$  OTSeo conversion (and possibly addi-137 tional regular liberation of oxygen<sup>5</sup>) being confined to 138 surface regions of the target facing the hydrophilic re-139 gions of the stamp: 140

STAMP reaction (cathode):  $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$  141

TARGET reaction (anode):  $-CH_3+2H_2O \rightarrow -COOH +$  142  $2H_2+2H^++2e^-$  143

overall process: $-CH_3(TARGET) +$				
$2H_2O \rightarrow -COOH (TARGETeo) + 3H_2$	145			

In principle, this water-mediated process thus offers 146 a straightforward means for the direct replication of information stored on a smooth silicon surface in the form of wetting contrast between the hydrophilic and hydrophobic domains of a patterned organic monolayer assembled on it, regardless of how the initial hy-151

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drophilic @ hydrophobic monolayer pattern was created. Here, water plays the essential triple role of electrochemical reagent, electrolyte, and conformal information transfer medium facilitating uniform transfer of information between the contacting surfaces involved in the electrochemical process, despite the inherent inability of two rigid surfaces to establish intimate molecular contacts over macroscopic geometrical areas of contact.<sup>3</sup> The resulting electrochemical transformation is thus effectively confined to the interfacial water bridges connecting the two surfaces, dry points of contact remaining inactive. Consequently, to ensure faithful pattern replication, the formation of such water bridges needs to be strictly confined to the hydrophilic features of the stamp.

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167 While the basic feasibility of the CER process 168 has been demonstrated, the preliminary results 169 obtained in the proof-of-concept experiments re-170 ported previously<sup>31</sup> were far from satisfactory, 171 172 apparently because of poor selectivity in the confinement of water bridges to the hydrophilic re-173 gions of the stamp pattern. As surface condensa-174 tion from the ambient was also employed for 175 the optical imaging of both the stamp and rep-176 177 lica patterns, insufficient selectivity in the preferential condensation of water on hydrophilic 178 monolayer features further contributed to the ap-179 parent low quality of the information transfer in 180 these first CER experiments.<sup>31</sup> Here we show how 181 182 these difficulties may be overcome so as to achieve high fidelity in the contact electrochemical replication 183 of hydrophilic @ hydrophobic monolayer patterns. This 184 paper is devoted to a comprehensive study of the rep-185 186 lication of hydrophilic monolayer features spanning lateral dimensions in the micrometer-centimeter range, 187 which allows an unequivocal chemical-structural char-188 189 acterization, by the combined application of optical imaging, SFM, and quantitative FTIR (Fourier transform in-190 frared) and micro-FTIR spectroscopy, of both the stamp 191 and corresponding replica patterns. Issues of spatial 192 resolution as well as the possible extension of the CER 193 194 approach down to the nanoscale are outside the scope of this work and will be addressed in future 195 publications. 196

### RESULTS AND DISCUSSION

198 Fabrication of Monolayer Stamp Patterns. Monolayer stamp micropatterns exposing well-defined hydro-199 philic and hydrophobic features, in terms of their mo-200 lecular structure and surface-exposed functionality 201  $(-COOH and respectively -CH_3)$ , were fabricated as 202 depicted in Figure 2, by mask-defined local photocleav-203 age of the alkyl tails of a self-assembled OTS/Si 204 monolayer,<sup>6,32,33</sup> followed by back filling of the empty 205 spaces thus created with a self-assembled NTS/Si 206 monolayer (NTS/Si denotes a monolayer derived from 207

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Figure 2. Fabrication of hydrophilic @ hydrophobic monolayer micropatterns for use as CER stamp patterns with well-defined molecular structure and surface functionality: Local removal of the alkyl tails of a self-assembled OTS/Si monolayer, *via* photocleavage in areas selected by UV irradiation through a TEM (transmission electron microscope) grid employed as contact mask (A, B), is followed by self-assembly of NTS in the irradiated areas (C) and final conversion of NTS to NTSox (oxidized NTS) *via* wet chemical oxidation of its terminal vinyl group to –COOH (D). The resulting monolayer pattern (NTSox@OTS) consists of hydrophilic NTSox/Si squares and hydrophobic OTS/Si bars, surrounded by a hydrophobic OTS/Si monolayer background.

the nonadecenyltrichlorosilane, SiCl<sub>3</sub>—(CH<sub>2</sub>)<sub>17</sub>— CH—CH<sub>2</sub>, molecular precursor<sup>2,4,7,15</sup>), and final conversion of NTS to NTSox (oxidized NTS) *via in situ* chemical oxidation of its terminal vinyl function to -COOH.<sup>4</sup> As shown in Figure 3, this pattern fabrication route can yield good monolayer patterns with rather sharp boundaries (on a micrometer scale) between OTS (hydrophobic) and NTSox (hydrophilic) surface regions, as



Figure 3. Example of a variable TEM grid with four different quadrants (SPI, GVHS Fine Square Mesh, Nickel) used as contact mask in the pattern fabrication process (steps **A** and **B** in Figure 2), and SFM images of two regions of the final NTSox@OTS monolayer micropattern (step **D** in Figure 2) corresponding to the two yellow frames in the optical image of the central region of the TEM grid. The metal bars of the grid have constant width while the widths of the square holes vary from one quadrant to the other. As expected, the contrast in the lateral force SFM images is indicative of higher friction within the hydrophilic NTSox squares compared to the hydrophobic OTS bars.<sup>2,3,16</sup>

## Monolayer Prints of TEM Grids



Figure 4. Examples of optical micrographs of water condensation patterns generated by preferential condensation under precise humidity and temperature control (in a specially built humidity cell) on the hydrophilic OTSeo regions of OTSeo@OTS monolayer patterns produced electrochemically on OTS/Si monolayers with TEM copper grid stamps (CML process).<sup>3</sup> The electrochemical printing was done with a voltage bias of 10 V (stamp negative, target ground) applied for 10 s while manually pressing the TEM grid stamp against the OTS/Si target (with the help of an eraser-caped pencil), immediately after brief exposure of the grid to saturated water vapor above a beaker filled with hot water. Currents of the order of 5 mA were measured during the printing of the patterns. Since such monolayer patterns are not optically visible in the absence of surface condensed water, scratch markers help locate them on the surface of the target (indicated by the two yellow arrows).

defined by the metal bars and, respectively, square holes of the contact mask used in the photocleavage patterning step (Figure 2, A and B).

WATER — Its Key Role and Limitations. Monolayer stamp patterns fabricated by the procedure depicted in Figure 2 have been tested in a series of exploratory CER experiments conducted with the purpose of identifying experimental conditions under which high-fidelity replicas may be obtained. Using a purpose-designed cell that allows fine control of both the environmental relative humidity (RH) and surface temperature (within  $\sim$ 5% RH and  $\pm$  0.1 °C; see Experimental Section), it became possible to generate water condensation patterns of dramatically improved quality (compared to those previously reported)<sup>31</sup> via preferential condensation on the hydrophilic features of hydrophilic @ hydrophobic monolayer patterns of the kind employed as stamps or obtained as replicas in the CER process (Figure 4). However, while such water/monolayer conden-

sation patterns serve well the purpose of optical imag-235 ing of the respective underlying monolayer patterns 236 (which by themselves are not optically visible), their 237 performance as CER stamps is, in general, limited. Like 238 any liquid, plain liquid water is incompressible and so 239 may perform well as information transfer medium in the 240 CER process only as long as a water film of uniform 241 thickness forms on all hydrophilic features of the mono-242 layer stamp pattern, regardless of their lateral dimen-243 sions and shapes. In general, this is a rather improbable 244 situation. Water is volatile and its high surface tension 245 favors the formation of guasi-spherical (droplet-like) 246 features,<sup>34</sup> as also indicated by the appearance of the 247 crossing points of the water bars in the bottom image 248 in Figure 4. Thus, it is practically impossible to generate 249 stable water patterns of uniform thickness on top of hy- 250 drophilic monolayer features with variable lateral di-251 mensions and aspect ratios. Moreover, one cannot eas-252 ily follow and so control the formation of water patterns 253 with dimensions below those accessible by optical mi-254 croscopy, while the characterization of liquid features 255 by SFM techniques is difficult and rather impractical for 256 our purpose.<sup>10</sup> Although in general unlikely to yield sat- 257 isfactory results, plain liquid water was successfully em-258 ployed as information transfer medium in a CER experi-259 ment carried out with the purpose of providing direct 260 spectral evidence on the nature of the monolayer trans-261 formation induced by a uniform macro-size NTSox/Si 262 monolayer stamp in a target OTS/Si specimen of com-263 parable dimensions (ca. 3.5 cm  $\times$  2 cm), which is well 264 suited for acquisition of quantitative infrared spectra in 265 the Brewster angle configuration<sup>35,15</sup>(Figure 5). 266

The main spectral features of interest in Figure 5 267 are the 2964 cm<sup>-1</sup> and 2879 cm<sup>-1</sup> methyl bands of 268 OTS<sup>15,35</sup> (curve a), which are missing in both NTSox and 269 OTSeo spectra (curves b and c), the identical peak posi- 270 tions and band widths, and almost identical peak absor- 271 bance of the 2917, 2850, and 1467  $\text{cm}^{-1}$  methylene 272 bands<sup>15,35</sup> in all three curves, and the similar -COOH 273 bands around 1718 cm<sup>-1</sup> in the NTSox<sup>15,35</sup> and OTSeo 274 curves. These observations unequivocally demonstrate 275 that the electrochemical transformation converting 276 OTS/Si to OTSeo/Si is limited to the top  $-CH_3$  groups 277 of OTS only, which are quantitatively oxidized to 278 -COOH with full preservation of the molecular organi-279 zation of the inner core of the monolayer. Thus, the alkyl 280 tails in OTSeo/Si retain the extended all-trans conforma-281 tion, perpendicular orientation, and dense, solidlike 282 packing characteristic of its OTS/Si precursor and simi-283 lar highly ordered organosilane monolayers.<sup>15</sup> The 284 small decrease in the peak absorbance of the  $-CH_2$ -285 stretch bands around 2900 cm<sup>-1</sup> upon the conversion 286 of OTS to OTSeo may be indicative of some damage 287 caused to the reacted monolayer in this particular 288 sample,<sup>36</sup> possibly at points of closer contact and 289 higher local electrical fields and current densities than 290 the average (vide infra), which does not, however, affect 291

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its overall molecular organization. 292 293 Finally, by comparison with NTSox (curve b), one may note the missing 294 shoulder at  $\sim$ 1734 cm<sup>-1</sup> in the 295 C=O stretch band of OTSeo (curve 296 c), assigned to monomeric -COOH 297 species.<sup>15,35,37</sup> It thus appears that 298 the organization of the top -COOH 299 groups of OTSeo is not identical to 300 that of NTSox, the former possibly 301 302 exhibiting more extensive lateral hydrogen bonding between adja-303 cent acid groups.35,37 304

One may note that although 305 the applied voltage bias in this CER 306 experiment (40 V) was significantly 307 higher than that normally used in 308 the CNL patterning with conductive 309 SFM tips (3-17 V),<sup>2,7,16,14</sup> in the av-310 erage, the measured current den-311 312 sity is here between 2 and 3 orders of magnitude lower. In both cases, 313 the structural stability of the mono-314 layer upon the application of the 315 voltage bias suggests that the effec-316

317 tive voltage drop across the monolayer itself may not exceed 3-4 V-the expected threshold of dielectric 318 breakdown in such films.<sup>38</sup> With a printed monolayer 319 area of  $\sim$ 7 cm<sup>2</sup> the maximal measured current density 320 of  $\sim$ 96  $\mu$ A/cm<sup>2</sup> (670  $\mu$ A/7 cm<sup>2</sup> (assuming uniform cur-321 rent over the entire geometrical area of contact be-322 tween stamp and target) translates into  $\sim$ 0.192 fA/200 323 nm<sup>2</sup>, which is the equivalent current passing through a 324 surface area comparable to that usually covered by a 325 conductive SFM tip in contact with the monolayer sur-326 face in the CNL process.<sup>14</sup> Typical onset writing currents 327 in CNL were found to be of the order of 100 fA, that is, 328 current densities ca. 520 times higher than that mea-329 sured in this CER experiment. A current density of 330  $\sim$ 0.192 fA/200 nm<sup>2</sup> further translates into  $\sim$ 1.92  $\times$ 331  $10^{-4}$  fA/OTS molecule, or ~1.2 electrons/s/OTS mol-332 ecule (with 0.2 nm<sup>2</sup> as the molecular area of OTS in a 333 compact, highly ordered monolayer<sup>15,35</sup>). This corre-334 sponds to a total charge of  $\sim$ 72 electrons passing in 335 the average through a single OTS molecule during the 336 1 min printing time. For comparison, in dots inscribed 337 with 3.0 ms voltage pulses applied to a scanning tip,<sup>7</sup> 338 the total charge passing through a single OTS mono-339 layer at a current density of  $\sim$ 100 fA/200 nm<sup>2</sup> (*i.e.*,  $\sim$ 1.0 340  $\times$  10<sup>-1</sup> fA/OTS molecule)<sup>39</sup> is ~1.9 electrons, which is 341 the actual limiting charge (2 electrons) required for the 342 electrochemical oxidation (with a 100% yield) of a single 343 344  $-CH_3$  group to -COOH (vide supra). This analysis suggests that the printing time under 345

Inis analysis suggests that the printing time under
 experimental conditions like those indicated in Figure
 6 might be reduced from a minute to less than 2 s. How ever, regardless of whether the printing time is 2 or



Figure 5. Quantitative Brewster angle FTIR spectra<sup>35,15</sup> of macrosize OTS/Si target (a, black curve), NTSox/Si stamp (b, blue curve), and OTSeo/Si replica (c, red curve) produced upon the application, for 1 min, of a bias voltage of 40 V between stamp (negative) and target (grounded), the entire CER operation being carried out in a humidity-temperature controlled atmosphere at ~100% RH, 22 °C, using a weight of 1.3 Kg to press the stamp against the target. Currents varying between ~670  $\mu$ A (initial) to ~400  $\mu$ A (final) were measured during the application of the voltage bias, with a geometrical area of contact between stamp and target of ~7 cm<sup>2</sup> (see text). The curves represent net spectral contributions of the organic monolayers, after mathematical subtraction of the spectral contributions of the respective bare Si substrates. Since both the stamp and target monolayers were assembled on double-side-polished wafer substrates (see Experimental Section) while the OTSeo/Si replica is the result of an electrochemical transformation that affects only the printed side of the OTS/Si target, to facilitate a direct comparison, all spectral curves were normalized to the corresponding one-side contributions. In the spectral range 1900–1300 cm<sup>-1</sup>, the blue and red curves are shifted vertically for clarity.

60 s, the advantage of parallel (one-step) printing of an entire pattern as compared to its serial inscription with a scanning tip should be evident if one realizes that to fill an area of 7 cm<sup>2</sup> (*i.e.*,  $7 \times 10^{14}$  nm<sup>2</sup>) with a scanning tip inscribing individual dots at the speed of 200 nm<sup>2</sup>/3.0 ms would require  $1.05 \times 10^{10}$  seconds, the unrealistic time of 332 years!

**Quasi-Water Patterns.** To overcome the fundamental obstacles encountered in the utilization of plain liquid water as information transfer medium in the CER process, we undertook a research strategy based on the hy-





Figure 6. Wetting driven self-assembly (WDSA): Selective retention of a nonvolatile liquid (neat, solution, melt) with appropriate surface tension on the wettable (lyophilic) portion of a monolayer pattern consisting of wettable regions surrounded by a nonwettable (lyophobic) background is achieved upon slow retraction of the monolayer-coated substrate from the liquid.<sup>14</sup> The speed of retraction is conveniently regulated with the help of a motor-driven lift.



Figure 7. Like water, agarose or glycerol can be selectively and reversibly immobilized on the hydrophilic regions of NTSox@OTS monolayer patterns. Because of rapid evaporation, the formation (by surface condensation) and conservation of such water/ monolayer patterns demand precise humidity and temperature control. Unlike water, glycerol/monolayer and agarose/monolayer micropatterns are stable, and so can be easily fabricated by WDSA (Figure 6) and erased by dissolution in water and aqueous HCI. The "agarose; glycerol/(NTSox@OTS) Micropattern" used to illustrate the WDSA process is the actual micrograph of an agarose/monolayer micropattern produced in this manner.

> pothesis that water might be replaced by water absorbing materials (WAMs) that can simulate water as far as the formation of effective electrolyte bridges in the CER process is concerned, while differing from plain liquid water in a number of other desirable properties. Useful WAMs are thus expected to have low volatility, adhere selectively to the hydrophilic regions of a hydrophilic @ hydrophobic monolayer pattern forming WAM/monolayer patterns of variable dimensions and aspect ratios, and be compressible and easily removable from the surface (to allow repeated utilization of the underlying monolayer pattern).

> Here we present proof-of-concept experimental results obtained with two very different WAMs, selected with the purpose of identifying similarities as well as expected differences in their modes of action: glycerol, a low molecular weight hygroscopic liquid, and agarose, a high molecular weight polysaccharide polymer forming thermoreversible hydrogels.<sup>42</sup> Both glycerol and dilute aqueous solutions of agarose do not wet methylrich hydrophobic surfaces such as that of a highly ordered OTS monolayer but adhere well to the top -COOH groups of NTSox or NTSeo, thus facilitating their selective immobilization on the hydrophilic regions of NTSox@OTS stamp patterns or NTSeo@OTS replica patterns. This is easily achieved by wetting driven self-assembly (WDSA),<sup>14</sup> using the simple experimental setup depicted in Figure 6.

> Glycerol was assembled from the neat liquid at the ambient temperature ( $22 \pm 0.5$  °C), and agarose was obtained from a diluted water solution at 90 °C (see Experimental Section). Upon cooling down and equilibrating with the ambient humidity (RH 50 ± 5%), agarose forms stable hydrogel/monolayer patterns. Due to its low volatility (bp 290 °C), glycerol forms stable liquid/ monolayer patterns as well. Thus, unlike water, both glycerol/monolayer and agarose/monolayer stamp pat-

terns are stable and easily handled in ambient 397 conditions without the need of providing pre-398 cise humidity and temperature control (Figure 399 7). Glycerol is easily removed from the mono-400 layer pattern by dissolution in water, and aga-401 rose by dissolution in hot water and aqueous 402 HCI (see Experimental Section). As discussed in 403 the following, the essential difference be-404 tween glycerol and agarose is that glycerol, 405 like water, is an incompressible liquid, while 406 agarose hydrogel is a hydrated polymeric net-407 work that resembles a flexible water-absorbing 408 sponge which may reversibly swell and con-409 tract to a certain extent without loosing its wa-410 ter content. 411

WAMs Performing Better than Water. Exploratory412CER experiments have been carried out with413the main purpose of verifying our basic hy-414pothesis regarding the possible utilization of415WAMs as effective information transfer media416

in the CER process. At this stage, no attempt was made 417 to standardize or optimize the experimental protocol, 418 many details of which being varied rather drastically 419 from one experiment to another (vide infra) in order to 420 gather data that would allow us improve our under-421 standing of the CER mechanism toward its future opti-422 mization. The main results of two successful CER experi-423 ments, representative of glycerol and agarose, are 424 discussed in the following. 425

Glycerol. Exploiting the stability of glycerol/mono-426 layer patterns, glycerol was successfully applied both 427 as an information transfer medium in the CER process 428 and as a visualization developer in the optical imaging 429 of the resulting replica patterns. High quality replicas, 430 virtually identical to the corresponding stamp patterns, 431 were obtained (Figure 8), which attests to the high fidel-432 ity of the glycerol-mediated replication process. The 433 presence of water in glycerol is clearly revealed (in the 434 infrared spectra) by the characteristic water bending 435 mode<sup>43</sup> at 1654 cm<sup>-1</sup>, as well as by the much stronger 436 band around 3344  $\text{cm}^{-1}$ , which contains contributions 437 from both water<sup>43</sup> and the alcohol O–H groups of the 438 glycerol<sup>44,45</sup> itself. One may note that although the FTIR 439 microscope was purged with dry nitrogen, no decrease 440 in the intensities of the water bands was observed dur-441 ing the collection of these IR spectra, which points to 442 the high affinity of glycerol for water and, consequently, 443 to its effectiveness as a water-immobilizing agent un-444 der regular ambient conditions. 445

Besides its value as a rather unique tool for the direct monitoring of the water content of surfaceimmobilized thin films, quantitative FTIR microscopy 448 was found particularly useful in the nondestructive 449 evaluation of the relative thickness of such liquid films. 450 According to the ratios of the -C- peaks (at 2936 and 451 2882 cm<sup>-1</sup>) and the water peaks (at 1654 cm<sup>-1</sup>) in the 452 glycerol IR spectra (Figure 8), the liquid squares in pat-

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Figure 8. (Top) Optical micrographs of glycerol/(OTSeo@OTS) monolayer replica patterns fabricated by the CER process (Figure 1) with stamps consisting of glycerol/(NTSox@OTS) monolayer micropatterns (Figure 7). Replica A was generated with a voltage bias of 20 V applied for 1 min (measured current ~250  $\mu$ A) and replica B with 40 V applied for 30 s (measured current 250–300  $\mu$ A), both under ambient conditions (~50% RH, 22 °C), with the stamp negative and the target grounded. No external pressure was applied between stamp and target. The stamp (not shown) and respective replica patterns (A and B) are practically indistinguishable. (Bottom) Representative micro-FTIR spectra collected from a single square of pattern A and a single square of pattern B (see Experimental Section).

454 tern A are 4.6-4.9 times thicker than those in pattern B. As it has been found in WDSA experiments with both 455 glycerol<sup>46</sup> and other liquids (unpublished results), the 456 thickness of liquid features immobilized by this process 457 on a patterned surface scales up in a rather complex 458 459 manner with the lateral dimensions of the wettable surface features to which the liquid adheres, implying 460 that monolayer patterns with variable size of wettable 461 features retain liquid films of variable thickness, de-462 pending (among a number of additional parameters) 463 on the relative lateral dimensions of the respective pat-464 tern features.<sup>46</sup> This limits the usefulness of liquid 465 WAMs such as glycerol to the case of monolayer pat-466 terns with wettable features of uniform size, like pat-467 terns A and B in Figure 8. The replication of monolayer 468 patterns with wettable regions differing significantly in 469 their lateral size was found to suffer from either or both 470 the coalescence of adjacent liquid features and the mis-471 472 match of their different heights in the stamping process. Because of liquid incompressibility, applying exter-473 nal pressure to the stamp in an attempt to establish 474 stamp-target contact in pattern regions with low liquid 475 thickness necessarily results in spillover of the taller liq-476 477 uid features, thus compromising the entire replication process. 478

*Agarose Hydrogel.* Experimental data pertaining to some
 relevant aspects of the structure and composition of a
 representative agarose/(NTSox@OTS) monolayer micro-

pattern with variable size of wettable features are summarized in Figure 9. Like in the case of glycerol (Figure 8), the thickness of the agarose features is seen to scale up with their lateral dimensions. One may note that the thickness ratio A/B measured by SFM (200 nm/60 nm = 3.33) compares well with the ratios of each of the absorbance peaks in the IR spectra of squares A (red curve) and B (black curve): 3.5 (3418), 3.1 (2918), 3.3 (1647), 3.3 (1072 cm<sup>-1</sup>). As the bands at 1072 and 2918 cm<sup>-1</sup> represent -C-OH and -C-H agarose vibrational modes, respectively,  $^{44,45}$  the 1647 cm<sup>-1</sup> band is the characteristic bending mode of water,<sup>43</sup> and the 3418 cm<sup>-1</sup> band contains contributions from the O–H stretching vibrations of both water<sup>43</sup> and agarose,<sup>44,45</sup> these findings point to a very similar distribution, structure, and concentration of water in all these microgel features, regardless of their overall dimensions.

With a molar absorption coefficient of 21.8  $\pm$  0.3  $M^{-1}$  cm<sup>-1</sup> (determined for the bending mode of bulk water at 1643 cm<sup>-1</sup>),<sup>43</sup> the measured peak absorbance at 1647 cm<sup>-1</sup> corresponds to a water layer thickness of 41.4  $\pm$  0.6 nm in square A and 12.4  $\pm$  0.2 nm in square B. This accounts for 20–21% of the total SFM-measured thickness of each of these microgel features. Since both the SFM and IR data in Figure 9 were obtained at ~55% RH, this figure applies to the agarose microgel in equilibrium with an atmosphere maintained at a relative humidity around 55%. Variations in the ambient humidity

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Figure 9. Combined application of optical microscopy, SFM, and quantitative micro-FTIR spectroscopy in the characterization of a typical agarose/(NTSox@OTS) monolayer micropattern with variable size of wettable features. Optical microscopy was used to select two agarose squares, A and B, which were then imaged by SFM and their IR spectra recorded with an FTIR Microscope. Squares A and B are seen to differ considerably in their heights (as indicated by both the interference colors in the respective optical images and the corresponding SFM topographic images and IR absorbance intensities), which scale up with their lateral dimensions. There is good agreement between the heights ratio A/B measured by SFM and the ratios of the absorbance peaks in the IR spectra of squares A and B (recorded with 60  $\mu$ m  $\times$  60  $\mu$ m and 40  $\mu$ m  $\times$  40  $\mu$ m microscope apertures, respectively). The IR spectra further allow a quantitative estimation of the water content of the agarose features (see text).

were found to affect the water content of the agarose microgel features accordingly. For example, at ~10% RH, the water content of same agarose squares was found to drop to 7–10% of their total SFM-measured thickness, which shrinks to 83–85% of that at ~55% RH (see Supporting Information, Figures S1 and S2).<sup>47</sup>

Experimental results summarized in Figures 10-12 demonstrate the successful high-fidelity replication of a monolayer micropattern with variable size of wettable features (like that of Figure 9) using agarose hydrogel as information transfer medium in the CER process. The faithful replication of the monolayer stamp pattern is confirmed by comparing the lateral dimensions of the different squares of the monolayer stamp pattern (Figures 3 and 10) with the corresponding squares of the bilayer @ monolayer pattern (Figure 11) and those of the bilayer @ monolayer pattern generated by the selective self-assembly of an organized top monolayer on the hydrophilic squares of the replica (Figure 12).

One may note in Figure 10 (images 2 and 3) the contraction/swelling of the agarose features under exposure to variable ambient humidity (also see Supporting Information, Figures S1 and S2) as well as 532 the fact that replication could be achieved 533 only with the hydrogel stamp at 100% 534 RH. It thus appears that only the fully swol-535 len agarose gel can function as an effec-536 tive electrolite bridge in the CER process; 537 however, even under such conditions the 538 gel is sufficiently compressible to allow 539 faithful replication of surface features of 540 significantly different dimensions. This re-541 markable performance suggests that the 542 agarose stamp features can indeed sus-543 tain considerable vertical deformation 544 without significant lateral expansion, 545 which points to a sponge-like structure 546 reminiscent of that of certain anisotropic 547 polymer brushes.48 548

The transfer of the pattern from the 549 stamp to the target surface following the 550 application of the voltage bias is immedi-551 ately apparent owing to the expected re-552 distribution of the agarose hydrogel be-553 tween the hydrophilic features of the 554 stamp and replica patterns. This is clearly 555 visible in optical micrographs taken imme-556 diately after the separation of the two 557 contacting surfaces (not shown). To ob-558 tain the water condensation image and 559 the SFM images of the bare replica (im-560 age 4 in Figure 10 and Figure 11) as well 561 as reuse the monolayer stamp pattern, the 562 hydrogel coating had to be removed by 563 soaking in boiling water and aqueous HCl 564 (see Experimental Section). Following 565 such treatment, the monolayer stamp pat-566

tern employed in this particular experiment could be 567 successfully reused in many CER experiments, carried 568 out over a period of time of several months. No struc-569 tural deterioration of the NTSox monolayer within the 570 hydrophilic squares of the stamp could be detected by 571 comparing micro-FTIR spectra recorded (as in Figure 11) 572 before and after its multiple reuse. A systematic investi-573 gation of the stability of repeatedly reused monolayer 574 stamp patterns as well as of the reproducibility of mul-575 tiple replication of a given monolayer pattern remains, 576 however, to be performed. 577

As expected on the basis of previous CNL and CML 578 results,<sup>2,3,7,10,16</sup> the lateral force (friction) within the hy-579 drophilic OTSeo squares of the replica is higher than 580 that measured within the hydrophobic OTS bars while 581 the corresponding topographic contrast is negative, 582 with the OTSeo squares appearing ca. 1.6 nm below 583 the OTS bars (Figure 11). The observed negative topo-584 graphic contrast of OTSeo versus OTS was shown to rep-585 resent an artifactal effect of the SFM imaging<sup>3,7,16</sup> rather 586 than the result of eventual structural damaging of the 587 monolayer within the printed regions. This is unequivo-588

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589 cally confirmed here by both the quantitative IR spectra in Figures 11 and 12 and the SFM 590 images in Figure 12. As discussed before (Fig-591 ure 5), the virtually identical methylene bands 592 of OTSeo and OTS, with peak positions at 2916 593 and 2849 cm<sup>-1</sup> (Figure 11), indicate that OT-594 Seo, like OTS, is a compact, highly ordered 595 monolayer with all-trans conformation and 596 perpendicular orientation of its hydrocarbon 597 tails. The conversion, within the OTSeo 598 squares, of the top  $-CH_3$  groups of OTS to 599 -COOH is evident from the diminished 600 methyl peak absorbance at 2954  $\text{cm}^{-1}$ , the re-601 sidual observed intensity being contributed 602 by the methyls of the OTS monolayer on the 603 604 back side of this silicon wafer substrate.

That the conversion of  $-CH_3$  to -COOH605 within the OTSeo squares is practically quanti-606 tative while the tail methylenes remain intact 607 can be directly deduced from an inspection of 608 609 the infrared spectra in Figure 12, where the complete disappearance of the methyl peak 610 at 2956  $cm^{-1}$  is clearly identified on the 611 methyl-free background contributed by the 612 NTS monolayers present here on both sides 613 614 of the silicon substrate. Finally, the assembly 615 of a top NTS monolayer on OTSeo is seen to result in a proportional growth of the methyl-616 ene bands, their invariant widths and peak po-617 sitions at 2916 and 2849 cm<sup>-1</sup> bearing 618 619 evidence for the formation of a complete, highly ordered top monolayer, structurally in-620 distinguishable from the bottom OTSeo or OTS mono-621 layers. This conclusion is corroborated by the measured 622 topographic difference of  $\sim$ 2.7 nm between the bi-623 layer and monolayer pattern features (Figure 12), as ex-624 pected for a compact and well-ordered NTSox mono-625 layer covering the OTSeo regions.<sup>7,15</sup> Thus, unlike the 626 apparent depth of the hydrophilic OTSeo squares in the 627 OTSeo@OTS monolayer pattern (Figure 11), the hydro-628 philic NTSox/OTSeo bilayer squares in the NTSox/ 629 OTSeo@OTS pattern (Figure 12) display normal posi-630 631 tive topographic contrast along with the expected higher friction relative to the hydrophobic OTS bars. 632 While the reason for the different behavior of the hydro-633 philic bilayer and monolayer features remains to be 634 clarified, the consistency of the SFM and IR data in Fig-635 ure 12 would not be possible unless the negative topo-636 graphic contrast of OTSeo versus OTS in the 637 OTSeo@OTS replica pattern (Figure 11) were not an im-638 aging artifact. Furthermore, the self-assembly of a ho-639 mogeneous and highly ordered top monolayer on the 640 641 squares of the replica pattern implies that the squares must be covered by a homogeneous and highly or-642 dered OTSeo bottom monolayer template,<sup>7</sup> produced 643 by the (nondestructive) quantitative conversion of the 644 terminal -CH<sub>3</sub> groups of OTS to -COOH. 645



Figure 10. Optical micrographs demonstrating the high-fidelity replication of a NTSox@OTS monolayer micropattern with variable size of wettable features (the same monolayer pattern as in Figure 3) using agarose hydrogel as information transfer medium in the CER process: (1) water condensation image (as in Figure 4) of the NTSox@OTS monolayer micropattern; (2) agarose/(NTSox@OTS) micropattern (agarose hydrogel stamp) under normal ambient conditions (~50% RH, 22 °C); (3) same as panel 2 after equilibration with a saturated water atmosphere (100% RH, 19 °C) in the special humidity cell (hydrogel stamp at 100% RH); (4) water condensation image of the OTSeo@OTS replica pattern produced with the hydrogel stamp at 100% RH (with a voltage bias of 40 V applied for 30 s, the stamp being negative and the target grounded, measured current of  $250-300 \mu$ A, no external pressure between stamp and target). The replica 4 generated along path  $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$  is a high-fidelity mirror image of the initial monolayer pattern of panel 1. Direct  $1 \rightarrow 4$  pattern transfer, in the absence of agarose, does not yield comparable high quality replicas.

Some Control Experiments. A bias voltage of 40 V was applied for 1min to a pair of OTS/Si specimens (1 cm  $\times$  1 cm each) pressed together with a total external force of  $\sim$ 15 Kg, first in the ambient atmosphere (55% RH, 21-22 °C) and then in an high humidity atmosphere (96% RH, 21–22 °C). The measured currents,  $\sim$ 700  $\mu$ A at 55% RH and  $\sim$ 1540  $\mu$ A at 96% RH, are significantly higher than those recorded in the CER experiments discussed before (Figures 5, 8, and 10). Contact angle measurements complemented by quantitative infrared spectra and SFM images recorded before and after the application of the voltage bias unequivocally demonstrate that, regardless of ambient humidity, the OTS monolayers suffered no transformation or damage upon the application of the voltage bias. These results show that (i) significant electrical currents may pass through two contacting monolayer/Si specimens to which a voltage bias is applied also in the absence of interfacial electrolyte bridges that promote electrochemical monolayer transformations; (ii) large variations in the magnitude of the measured current can be expected depending on experimental variables such as applied voltage, applied mechanical pressure (effective area of contact), environmental humidity, and the nature and resistance of the contacts to the silicon specimens. It follows that establishing a correlation between

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Figure 11. SFM images showing the four different OTSeo squares of same OTSeo@OTS replica pattern as in Figure 10 and micro-FTIR spectra recorded (with a 75  $\mu$ m × 75  $\mu$ m microscope aperture) from one of the 150  $\mu$ m × 150  $\mu$ m OTSeo squares and from an equivalent unmodified OTS region of same specimen, which is representative of the OTS bars (bottom right). The notation OTSeo/Si + OTS/Si and OTS/Si + OTS/Si is used to indicate the fact that, being measured in transmission through the silicon wafer substrate, these IR spectra contain also the contribution of the back side of the wafer which is coated with a regular OTS monolayer. To enable visualization of the replica pattern and focusing of the IR beam on the desired surface site, the aperture of the FTIR microscope was superimposed on a water condensation image of the replica (*e.g.*, top right), the IR data being then collected after complete evaporation of the water.

the current measured in a particular CER experiment and the size and/or quality of the resulting monolayer replica pattern may not possible in the absence of effective control of each of these experimental parameters and a proper understanding of their interplay. These aspects of the CER process remain to be clarified in future work.

### **CONCLUDING REMARKS**

Taken together, the experimental results presented here establish contact electrochemical replication (CER) as a viable methodology for the direct electrochemical generation of copies of monolayer surface patterns consisting of hydrophilic domains surrounded by a hydrophobic monolayer background. The effective discrimination between wettable and nonwettable features of a monolayer pattern plays a central role in the CER process. Therefore, the use of highly ordered, defect-free OTS monolayers (exposing low-energy outer surfaces that are not wetted by a large variety of both aqueous and organic liquids — see Experimental Section) is a necessary precondition for its successful implementation.

As in the electrochemical printing with metal or other types of conductive stamps (*e.g.*, Figure 4),<sup>3,13,29,30</sup> the voltage-current relationship in the CER process and the related issue of the effective potential drop across the organic monolayers (target and stamp) are important open questions that remain to be ad-699dressed in future research. The different experimental700conditions tested in the course of this work and found701to yield good replica patterns (Figures 4, 5, 8, and 10)702provide a promising starting point, further work being703needed *en route* to a comprehensive rationalization of704the CER process and its optimization.705

While the full range of applicability of this method-706 ology remains to be established, there appears to be 707 virtually no upper limit to the size of hydrophilic fea-708 tures that can be copied by the CER process. Thus, CER 709 offers a simple novel route to the functionalization of 710 macroscopic surface areas via the straightforward con-711 version of exposed  $-CH_3$  groups of *n*-alkylsilane mono-712 layers to -COOH (Figure 5). As far as small pattern fea- 713 tures are concerned, high-fidelity replication down to 714 micrometer-sized features has been demonstrated here 715 by replacing plain liquid water with a compressible hy-716 drogel coating that acts as an effective guasi-water in-717 formation transfer medium in the CER process (Figure 718 10). The agarose hydrogel selected for this study is a 719 representative example of a water absorbing material 720 with the desired sponge-like properties; it is not neces-721 sarily the optimal choice of such materials. Given the 722 large variety of organic and inorganic hydrogels avail-723 able, the present promising results obtained with agar-724 ose pave the way to a systematic investigation of the 725 utilization of hydrogels for this purpose. 726

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If further developed and optimized, the CER
methodology is expected to offer a series of exclusive capabilities compared with other methods of surface patterning and bottom-up
assembly:

• CER is rather unique in that it is a printing 732 process enabling the direct copy of chemical in-733 formation from a monolayer surface (the "mas-734 ter") to another surface of the same kind, so 735 that, in principle, any replica could equally be 736 737 used as master in the printing of new such replicas. Consequently, multiple parallel reproduc-738 tion of a surface pattern, via the direct transfer 739 of information from one generation of replicas 740 to another, should become possible without the 741 742 need to repeatedly reuse an expensive and difficult to produce master in the fabrication of 743 each new replica. As demonstrated by the suc-744 cessful repeated reuse of the monolayer stamp 745 pattern used in the agarose-mediated CER ex-746 747 periment described here (Figures 3, 10, and 11), this may be achievable with highly stable ora-748 nosilane monolayer patterns which, unlike, for 749 example, alkanethiol monolayers on gold, 49,50 750 are not degraded even in rather harsh chemi-751 752 cal and electrochemical environments.

• CER operates on the sole basis of wetting 753 discrimination between the hydrophilic and hy-754 drophobic regions of a monolayer stamp pat-755 tern, using flat, rigid monolayer stamps, and 756 757 equally flat and rigid target surfaces consisting of a compact and extremely robust organosi-758 lane monolayer (OTS/Si) with an outer top sur-759 face that is both lyophobic (liquid repellent) and 760 chemically inert. Such patterns can be printed 761 762 on preassembled monolayer films covering the entire surface of the stamp or the target. These 763 features render CER compatible with a wide 764 range of postpatterning chemical modification 765 processes<sup>2,7,14</sup> that are further expected to be 766 767 free of lateral diffusion limitations of the kind encountered in  $\mu CP^{1,17,20}$  and  $DPN^{23,24}$  (which 768 also led to the advancement of flat<sup>20,21</sup> and 769 ink-free<sup>18,19</sup> versions of  $\mu$ CP). 770

• Because patterns are generated nonde-771 772 structively on a stable, densely packed, and highly ordered monolayer rather than destruc-773 tively (e.g., nanoshaving<sup>51</sup>) or by deposition of mate-774 rial on a bare surface that needs to be backfilled with 775 a second monolayer component which may par-776 tially displace the initially deposited material (e.g., 777  $\mu$ CP, DPN),<sup>1,17,24</sup> the CL–CER mode of patterning 778 appears ideally suited for the assembly of mono-779 layer template patterns with sharp, "seamless" 780 boundaries between the different components of 781 the pattern, as demanded by surface manipulation 782 with true molecular resolution. 783





• Being an inherently parallel method of patterning, CER is capable of fast processing of information regardless of the overall size of the pattern involved in the process. Extended down to the nanoscale, CER would provide a simple and straightforward means also for one-step replication of master nanopatterns serially created with a scanning probe or with an array of scanning probes;<sup>25</sup> with other words, CER would allow the unprecedented "upgrading" of a serial (slow) patterning process to a parallel (fast) one without losing

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the miniaturization advantage inherent in the serial process. Promising preliminary results in this direction, aiming at one-step electrochemical replication of tipinscribed monolayer nanopatterns, have recently been 797 obtained in this laboratory and will be reported in forthcoming publications. 799

**Water.** Water purity, particularly with respect to organic contaminants, plays a critical role in the preparation of highly hydrophilic surfaces such as those needed for the assembly of high quality silane monolayers<sup>15</sup> or in the fabrication of contact electrochemical stamps (*vide infra*). All operations involving the use of pure water were carried out with water freshly withdrawn from a Barnstead Nanopure Diamond UV/UF system equipped with a total organic carbon (TOC) monitor and fed with water prepurified by reverse osmosis, ion exchange, and passage through 1 and 0.45  $\mu$ m prefilters, which delivers ion-free and organic-free high purity water (18.2 M $\Omega$  cm, TOC less than 1 ppb).

Preparation of High Quality OTS/Si Monolayers. Cleaning of the Silicon Substrates. Silicon wafer substrates (Semiconductor Processing Co., Boston, double-side-polished, p-type, orientation <100> resistivity 8–11  $\Omega$  cm, 0.5 mm thick, cut into  $\sim$ 20 mm imes 40 mm or  $\sim$ 10 mm imes 40 mm strips) covered by their native oxide layer were cleaned by the following sequence of operations: the silicon strips (mounted in a special guartz holder) are first rinsed in a jet of pure water (to remove dust and silicon particles from the surface), then Soxhlet extracted with toluene for 30 min (to remove soluble organic impurities), and then subjected to a version of the first step of the RCA cleaning procedure,<sup>52</sup> consisting of immersion for 10 min in a mixture of 50 mL of pure H<sub>2</sub>O + 10 mL of NH<sub>4</sub>OH (25%) + 10 mL of H<sub>2</sub>O<sub>2</sub> (30%) in a quartz container thermostatted in a water bath at 68 °C. The RCA solution is guenched by overflowing it with pure water while the silicon strips remain submerged in liquid until the ambient temperature is reached, then the wet silicon strips are rapidly transferred to a beaker filled with pure water, rinsed under overflow for 10 min, and finally stored under pure water until use. To prevent contamination, the wafers must be cleaned shortly before the assembly of the monolayer. Silicon freshly cleaned by this procedure is perfectly hydrophilic (0° advancing and receding water contact angle) and so well suited for the assembly of high quality silane monolayers.<sup>15</sup>

Monolayer Self-Assembly. OTS/Si monolayers were assembled following a recently improved two-step procedure: (i) Freshly cleaned Si substrates, withdrawn from pure water and blown dry with clean, dry nitrogen withdrawn from a container of liquid nitrogen, are immersed for ca. 30 s in a 5 mM solution of OTS (Merck "For Synthesis" grade) in bicyclohexyl (BCH, Fluka, purified by percolation through basic alumina<sup>53</sup>) at 21-22 °C, followed by sonication for ca. 2 min in analytical-grade toluene (Frutarom). The immersion in the OTS/BCH adsorption solution and the toluene rinse are repeated once again. (Important: BCH was found to be ideally suited for use as solvent in the assembly of high-quality silane monolayers.<sup>15</sup>) OTS-covered surfaces prepared by this procedure emerge totally unwetted from the adsorption solution; (ii) elimination of monolayer defects by further densification and stabilization,<sup>7</sup> by exposure of the OTS-coated specimens for 12 h to a water saturated atmosphere (100% RH at 40 °C), followed by additional immersion in the OTS/BCH solution for ca. 30 s, sonication in toluene, and final annealing for 10 min in a preheated oven at 115 °C. This sequence of operations is repeated three times, ending with the thermal annealing at 115 °C.<sup>7</sup> All monolayer assembly operations were carried out at 50%–60% RH and 22  $\pm$  1 °C, in a humidity-temperature controlled vertical laminar flow hood (total-exhaust, Germfree Biofume, Class II). (Important: performing the monolayer assembly operations within this range of ambient humidity appears to optimize the thickness of the hydration layer present on hydrophilic silicon surfaces, which is a key parameter for successful assembly of high quality silane monolayers.<sup>15</sup>)

As determined by quantitative infrared measurements, densified OTS/Si monolayers assembled according to this experi-

mental protocol contain 3%-6% more OTS material then those 868 produced without densification (see Supporting Information, 869 Figures S3 and S4) and display hysteresis-free static contact 870 angles (equal advancing and receding values) of 116°-117° 871 with water, 57° with bicyclohexyl, and 53° with *n*-hexadecane. 872 These contact angle values are slightly but consistently higher 873 (by 1°-2°) then those measured on same OTS/Si monolayers 874 prior to their densification and stabilization. 875

Fabrication of the Monolayer Stamp Micropatterns. Photocleavage 876 Patterning Step (Figure 2A,B). TEM grids mounted in a Teflon holder 877 were cleaned by Soxhlet extraction with toluene, followed by ex-878 posure for  $\sim$  30 s to HNO<sub>3</sub> vapor, then thorough rinsed in pure 879 water (overflow) and finally dried in a stream of clean nitrogen. 880 A specially built stainless steel irradiation holder was used to im-881 mobilize and firmly press a freshly cleaned grid with its smooth 882 side against an OTS/Si specimen, the grid being covered with a 883 thin quartz window. UV irradiation (2 h,  $\lambda = 185$  nm) of the grid/ OTS/Si assembly (through a small aperture in the stainless steel holder) was performed in a UV cleaner equipped with Hq-vapor lamps (model NL-UV 253, NLE, Nagoya, Japan), under argon purge (Ar purity, 99.9999%), in order to maintain a clean environment and avoid formation of ozone and undesired growth of silicon oxide.<sup>6</sup> Irradiated specimens were stored overnight in 10% aqueous HCl, then thoroughly rinsed in pure water and finally cleaned by the same RCA procedure as the pristine silicon substrates (vide supra). Patterned monolayer specimens were stored under pure water until further use.

NTS Assembly and Conversion to NTSox (Figure 2C,D; Figure 12). The assembly of an NTS/Si monolayer in the irradiated areas of photopatterned specimens (Figure 2) was done in exactly the same manner as the first step in the procedure applied to the assembly of the OTS/Si monolayers (vide supra). Specimens were withdrawn from water and blown dry with clean nitrogen immediately before their immersion in the NTS/BCH solution. NTS (10% stock solution in chloroform) was obtained from Prof. K. Ogawa, Kagawa University, Takamatsu, Japan

In the case of bilayer assembly (Figure 12), specimens used after their optical and IR or SFM characterization were reconditioned by immersion for 2 h in 10% aqueous HCl, followed by thorough rinsing with pure water (overflow). No reconditioning was needed when the assembly of the top NTS monolayer followed immediately after the printing of the bottom OTSeo@OTS monolayer pattern.

The conversion of NTS to NTSox, *via* oxidation with the KM  $nO_4/crown$  ether (dicyclohexano-18-crown-6) complex in benzene<sup>4,35,53</sup> was done by immersion (for 12 h) in a 5 mM solution of the crown ether complex (Sigma, mixed isomers) in analytical grade bezene (Fluka) under dry nitrogen, followed by sonication (5–10 min) in clean benzene, immersion in 10% aqueous HCl for *ca*. 5 h, and then a final thorough rinse in pure water (overflow). Specimens were stored under water and used shortly after the conversion of NTS to NTSox.

**Glycerol/Monolayer Micropatterns.** The assembly of glycerol (J. T. Baker, anhydrous) on monolayer patterns was performed as depicted in Figure 6, by slowly pulling out (with the help of a motor-driven lift) the specimen bearing the monolayer micropattern from the neat liquid at the ambient temperature ( $22 \pm 0.5$  GC).

Agarose/Monolayer Micropatterns. Water solutions of agarose (ad-926 justed to a final concentration of 0.1 wt %) were prepared by dis-927 solving agarose powder (Sigma, type VII-A, low gelling tempera-928 ture, melting temp  $\leq$  65.5 °C) with stirring in pure water at the 929 ambient temperature and then heating up to 95 °C for 5 min. The 930 solutions were passed twice (at 60 °C) through a Millipore mem-931 brane filter (Durapore 0.1 µm) and then extracted at least four 932 times with 2-pentanol (at  $\sim$ 50 °C), to remove impurities (appar-933 ently surfactant compounds) that promote undesired surface 934 contamination of the OTS/Si monolayers with material from so-935

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lution. The bulk gelation of 0.1 wt % agarose solutions prepared by this procedure was found to occur at 16–21 °C, and is expected to shift toward higher temperatures as the concentration of surface-immobilized agarose features increases<sup>54</sup> upon loss of water by evaporation.

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The assembly of agarose on monolayer patterns was done from such freshly prepared agarose solutions at 90 °C, in the same manner as that of glycerol (*vide supra*).

The removal of agarose gel features assembled on NTXox or OTSeo monolayers, or transferred to the OTSeo replica features generated in the CER process with agarose stamps, was done by soaking for 2 min in pure boiling water and then in 10% aqueous HCl for 2 h at the ambient temperature, in order to remove a residual ultrathin layer of agarose that is not soluble in water. Preliminary IR data suggest that this water-insoluble residue may be a single monolayer of agarose bound covalently to the silane monolayer *via* ester bonds formed between the –OH groups of the agarose and the –COOH functions of NTXox or OTSeo.

Water Condensation Patterns. Control of the water condensation on the monolayer patterns was achieved in a specially built perspex cell equipped with a humidity sensor and a Peltier element that can be used to slowly vary the surface temperature of the specimen bearing the monolayer pattern and stabilize it within  $\pm$  0.1 °C. The relative humidity in the cell can be controlled within  $\sim$ 5% using a pair of small beakers filled with water or with various constant humidity salt solutions. A porous cellulose wick dipped into the liquid is used to increase the effective area of the liquid-vapor interface and so speed up the attainment of the equilibrium relative humidity. Continuous optical monitoring of the formation and disappearance of water patterns is realized (through a transparent glass window in the center of the perspex cover of the cell) with the help of a zoom lens system (Navitar) equipped with a digital camera connected to a computer.

Contact Electrochemical Replication Experiments. The CER experiments were carried out in a cell similar to that used for the control of the water condensation, equipped, in addition to the humidity sensor and the Peltier element, with stainless steel holders for the stamp and the target specimens that are electrically connected to a stabilized dc voltage generator, the output of which may be continuously varied in the range 3-80 V. We are experimenting with different types of electrical contacts to the stamp and the target. In the experiments reported here, pieces of flexible aluminum foil glued with adhesive tape were used to improve the holder-stamp and holder-target electrical contact; however, the effectiveness and reproducibility of electrical contacts is an important technical issue that remains to be addressed in future work. The upper holder (stamp) is mobile and may be pressed against the bottom holder (target) with variable mechanical force, manually or using calibrated weights. In-situ optical imaging of the stamp and target is not possible in this cell.

SFM Imaging. The wide scan SFM images (200  $\mu$ m  $\times$  200  $\mu$ m) needed in this study for the correlation of the SFM with the micro-FTIR data were acquired on an NTEGRA instrument (NT-MDT, Moscow, Russia) operated in the DualScan mode, which provides the option of simultaneous scanning by both sample and probe. In hydrogel experiments demanding deliberate variation of the ambient humidity, the sample compartment (equipped with a humidity sensor) was purged with dry or humidified nitrogen supplied from a RH-controlled humidifier specially built for this purpose.

Infrared Spectral Measurements. Quantitative FTIR spectra in the 999 Brewster angle configuration<sup>35</sup> (Figure 5) were acquired (at a 1000 resolution of 4 cm<sup>-1</sup>) as described before, <sup>35,53,15</sup> on a Nicolet 1001 1002 730 FTIR system equipped with a DTGS detector, wire grid ZnSe 1003 polarizer, and a computer controlled "shuttle" accessory that al-1004 lows automatic translation of the sample in and out of the IR 1005 beam during data acquisition. Quantitative micro-FTIR transmis-1006 sion spectra (Figures 8, 9, 11, 12) were acquired (at a resolution of 1007 4 cm<sup>-1</sup>) on a Bruker Equinox 55 spectrometer connected to an 1008 IRscope II infrared microscope accessory equipped with a liquid 1009 nitrogen-cooled MCT detector. The infrared microscope is also 1010 used as an optical microscope (equipped with a computerAll displayed spectral curves represent net spectral contributions of the respective surface coatings, after mathematical subtraction of the spectral contributions of the corresponding bare silicon substrates.

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Supporting Information Available: Humidity effects on agarose micropatterns; FTIR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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