New Approaches to Prepare Hydride Silica

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New Approaches to Prepare Hydride Silica

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Two synthetic schemes to produce a hydride-modified support that serves as an intermediate for the preparation of bonded phases for liquid chromatography (LC) and capillary electrophoresis (CE) are investigated. The strategies differ in the silane reagent utilized (trichlorosilane (TCS) or triethoxysilane (TES)) and the manner water is incorporated into the reaction. In the first approach, TCS in toluene reacts with a previously humidified silica substrate so that the reaction is confined to the silica surface. In the second approach, TES and a small amount of aqueous HCl are dissolved in THF, and this hydrolysate is diluted by a great factor in cyclohexane, prior to reaction with the silica substrate. Atomic force microscopy (AFM) images of the hydride film on wafers revealed that, unlike the traditional approach that produced a patchy coating, both new methods provided a homogeneous layer on the substrate's surface. IR and NMR spectra from porous silica particles clearly confirmed a successful surface modification. AFM and water contact angles (WCA) were used to examine the effect of dilution of the TES hydrolysate in cyclohexane on the trend of the film to polymerize on wafers and found that a dilution factor of at least 100 is required to attain a molecularly thin hydride layer. WCA and CE also revealed a strong susceptibility of the hydride silica intermediate to hydrolyze, even at low pH. Compared to TCS, the lower reactivity and volatility of TES resulted in a much more desirable experimental approach.

Chemically modified substrates, particularly silica, have been and continue to be widely used in liquid chromatography (LC) and capillary electrophoresis (CE) separations. Taking advantage of the high hydrolytic stability of the silicon−carbon linkage formed as well as its great versatility, the hydrosilylation reaction has been used over the last 2 decades for the preparation of hydride silica-based bonded phases:[1−11]

$$(1)$$
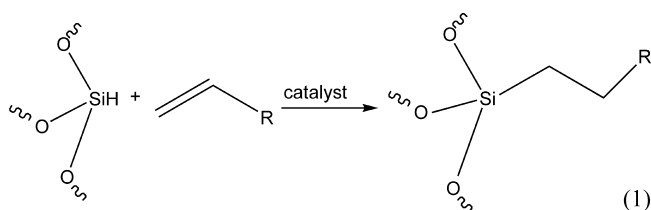
While the SiH groups required for the addition to occur can be produced by the chlorination of silica followed by reduction (both stages under strictly dry conditions),[1,2] the hydride silica intermediate can be much more conveniently prepared by the reaction of the surface silanol groups with TES, in the presence of water, HCl as catalyst, and dioxane as solvent, a process known as silanization:[3]

$$(2)$$
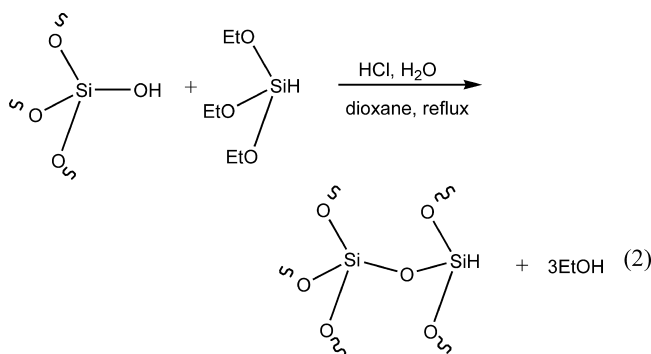
Under these conditions, extensive hydrolysis of the ethoxy groups of TES ($\equiv$Si−OEt → $\equiv$Si−OH + EtOH) and subsequent oligomerization of these (driven by silanol condensation, that is, $2\equiv$Si−OH → $\equiv$Si−O−Si$\equiv$ + H$_2$O) occur in the bulk solution as well as on the surface SiOH groups. While one would expect that the small steric hindrance from the hydride functionality results in maximum coverage of SiH groups, the possibility of multilayer formation is also very high. In fact, on the basis of atomic force microscopy (AFM) evidence from chemically modified CE tubes, Pullen et al. concluded that, under the conditions used in the former methodology, silanization with TES results not only in considerable SiH multilayer formation but also in the presence of patches of unreacted silica.[12] Such heterogeneity is obviously undesirable from a separation point of view (dual mode interactions have usually been considered

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unwelcome in many LC and CE separations), particularly when the hydride-modified substrate is used as a stationary phase.[13,14] Even though this limitation appears to be a serious one, virtually nothing has been reported on this issue. This paper thus explores two approaches aimed at solving this drawback to prepare the hydride silica intermediate. These alternate methods are based on the so-called "self assembled monolayer" (SAM) concept developed by Sagiv in 1980.[15]

SAMs are generally prepared by the reaction of trichloro alkylsilanes with a silica surface on which a monolayer of adsorbed water has been previously formed.[15−19] Since the different reaction events (hydrolysis and silanol condensation) are confined to the silica surface, the only place where water is available, extensive cross-linking of the silanol groups parallel to the silica surface ("horizontal polymerization") takes place, in preference to multi-layered structures ("vertical polymerization").[17,18] It should be pointed out that not only the amount of water used has to be limited to a monolayer, but also an easy-to-hydrolyze reagent such as a trichlorosilane must be used for the reaction to occur in the proper manner.[15−19] The result is a dense alkylsilane monolayer which exhibits a low silanol population. It has been claimed that SAM formation is driven by the development of siloxane linkages rather than the attractive interactions between adjacent alkyl chains.[16] In our first approach, a previously humidified silica substrate is allowed to react with TCS, $HSiCl_3$, dissolved in a hydrocarbon such as toluene:

$$ (3) $$
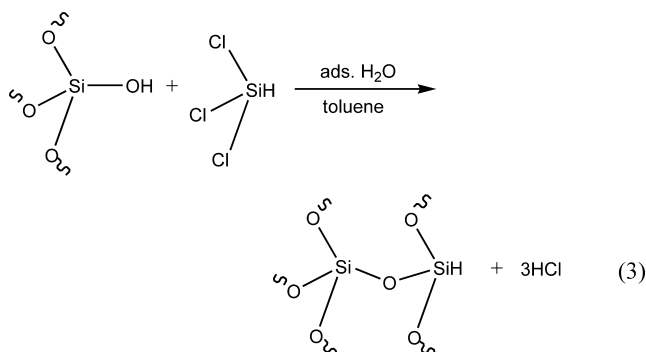
Although such a strategy had originally been devised for organosilanes bearing long hydrocarbon chains, the virtual absence of steric hindrance from the tiny hydride group makes the application of simple silanes of the type $HSiX_3$ especially attractive, provided that measures are taken to prevent bulk polymerization. The deposition of a water monolayer is realized by exposing the silica surface to an atmosphere of controlled relative humidity.[17−20] Since the reaction occurs exclusively on the silica surface, a substrate with a more homogeneous hydride coverage should result, in comparison to the current method described above.

In our second approach, a much less reactive silane such as TES, $HSi(OEt)_3$, is dissolved along with a small amount of aqueous HCl in a solvent such as THF. This reacting solution is diluted by a great factor (typically ≥100) in a nonpolar solvent such as cyclohexane, prior to the reaction with the silica substrate:

$$ (4) $$
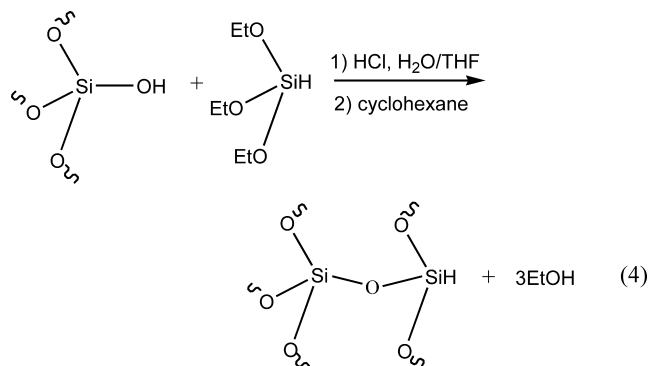
This approach is based on the methodology developed by Kessel and Granick to form alkylsilane SAMs on inorganic oxide substrates.[21] They used a prehydrolized trialkoxy (instead of trichloro) alkylsilane to effectively generate dense alkylsilane monolayers on mica. Huang et al. successfully extended this alternate SAM approach to the modification with vinyl-terminated hydrocarbon moieties of the inner surface of CE tubes.[22] Not only are alkoxysilanes much less susceptible to hydrolysis than chlorosilanes, but also the hydrolysis of the later generates HCl, which in turn furthers condensation reactions that easily lead to vertical polymerization. If measures are not taken to exclude water from the bulk solution, a polymeric network could be deposited on the solid substrate. Notice also that the use of a prehydrolyzed trialkoxysilane is required but not sufficient to obtain a suitable SAM; the choice of solvents is also of paramount importance for self-assembly. Although a polar solvent like THF is required to keep water and the silane undergoing hydrolysis in solution, a subsequent large dilution of the hydrolysate in a nonpolar solvent is critical for silane bonding to occur on the silica substrate. This extensive dilution should minimize ether−silanol interactions so that the much less coordinating hydrocarbon solvent enables a high-energy surface that provides the driving force required for a proper deposition to occur.[21]

EXPERIMENTAL SECTION

Apparatus. CE experiments were carried out in an Agilent model 3D CE System (Palo Alto, CA). IR spectra were taken with a Shimadzu model FTIR-8400 spectrometer (Columbia, MD) equipped with a diffuse reflectance infrared Fourier transform (DRIFT) accessory. NMR spectra were obtained with a Bruker Advance II-400 MHz NMR spectrometer (Rheinstetten, Germany) equipped with a Bruker MAS II probe. AFM images were obtained with an Asylum Research model MFP-3D-SA (Santa Barbara, CA) instrument. Rectangular silicon cantilevers with tetrahedral tips and nominal spring constants of 0.06 N/m were used. Image processing and roughness calculations were carried out using the

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Asylum Research software Igor-Pro 6. Homemade glass apparatuses were used to expose silica substrates to a controlled relative humidity (RH) provided by a saturated aqueous solution of selected salts.[23] For RH measurement purposes, a Sensirion AG model EK-H2 (Stäfa, Switzerland) kit equipped with a microprocessor board model ASD11 (including an LCD and RS-232 interface) and a Sensirion AG model SHT75 digital humidity sensor were used. Real-time monitoring of RH and temperature was achieved by means of the readout software HumiViewer version 3.0, supplied by the manufacturer as part of the kit. Static contact angle measurements with the sessile drop method[24] were recorded and analyzed at room temperature on a homemade goniometer consisting of a digital camera, a 10 μL syringe with unbeveled tip, a mini-jack stand, and a halogen lamp. ImageJ software (version 1.43), available at the National Health Institute Web site, along with a plug-in available at the Ecole Polytechnique Federale de Lausanne Web site were used to process drop images.[25]

Materials. Fused-silica capillaries of 50 μm i.d. were purchased from Polymicro Technologies (Phoenix, AZ). Corning 7980 fused-silica wafers (76.2 mm × 25.4 mm × 1 mm) were purchased from Bioindustrial Products (San Antonio, TX) and cut to 25.4 mm × 9 mm × 1 mm dimensions using a 22.2 mm × 0.22 mm silicon carbide disk obtained from Keystone Industries (Cherry Hill, NJ). Particulate silica (5 μm diameter and 75.4 m^2/g surface area) was obtained from Macherey-Nagel (Düren, Germany). 3-(N-morpholino) propanesulfonic acid (MOPS), tris(2,2′-bipy-ridine)ruthenium(II) chloride, and benzyl alcohol were purchased from Sigma-Aldrich (St. Louis, MO). Triethoxysilane and trichlorosilane were purchased from Alfa Aesar (Ward Hill, MA). All other reagents and solvents were of analytical grade and were obtained from various vendors. Although anhydrous solvents such as THF, cyclohexane, and toluene were purchased, they were freshly distilled from sodium shavings before use.

Silica Surface Conditioning. A 52 cm ×50 μm i.d. fused silica capillary tube was treated with a 1.0 M NaOH solution at 30 °C for 1 h, under 5.5 bar N$_2$ pressure.[26] After an extensive rinse with deionized water (1 h at room temperature), the tube was dried with 3 bar of dry N$_2$ for 2 h at 110 °C. Fused-silica wafers were conditioned in a similar manner. Porous silica particles did not undergo NaOH treatment but were dried at 110 °C for 4 h.

Surface Modification. In this work, we used three types of silica substrates: capillary tubes for CE experiments; wafers or plates to facilitate AFM and contact angle measurements by avoiding the drudgeries associated with the minute capillary dimensions; and porous particles to readily verify the success of hydride grafting by IR and NMR. Capillaries (typically, a 52 cm length) and wafers were treated under identical conditions, except that wafers were simply immersed in the reagent solution under gentle magnetic stirring, while the same solution was forced, by means of an applied pressure (typically, 5.5 bar of N$_2$), to continuous flow through the capillary. Because of their very

high surface area, porous silica particles required a significantly higher silane concentration to achieve an adequate silane-to-silanol molar ratio.

Silanization by New TCS-Method. The dried silica substrate was exposed to a 50% RH N$_2$ gas stream at room temperature (25 °C) for 1 h. A 50% RH was obtained by bubbling N$_2$ into a saturated calcium nitrate solution at 1 bar and room temperature. Continuous monitoring of RH was performed throughout the experiment. Subsequently, the humidified silica substrate was placed in contact with a 1.0 mM solution of TCS in toluene for 1 h at room temperature. Then, the substrate was rinsed successively with toluene and THF for 5 min each, at room temperature. Finally, the hydride silica was cured at 110 °C for 2 h under N$_2$.

Silanization by New TES-Method. A solution containing 50 mM TES, 5.0 mM HCl, and 0.15 M water in dry THF was allowed to hydrolyze for 30 min at room temperature under continuous magnetic stirring. The hydrolysate solution was then extensively diluted with cyclohexane and immediately placed in contact with the dry silica substrate for 30 min at room temperature. The reacting solution must be clear at all times; otherwise, the solvents must be redistilled from metal sodium to ensure close control of the water content during the process. The hydride silica was cured as described above after rinsing with THF for 10 min.

Silanization by Former TES-Method.[3] A solution containing 0.11 M TES, 2.3 M water, and 0.10 M HCl in dry dioxane was immediately placed in contact with the dried silica substrate and the temperature raised to 90 °C for 1.5 h. Rinsing and curing of the capillary was as described above for the new TES-procedure.

CE Characterization of Hydride-Modified Capillaries. Electroosmotic mobility (EOM) determinations followed a method previously described.[26,27] A 5.0 mM solution of benzyl alcohol in the MOPS background electrolyte solution was used as a neutral marker. The peak asymmetry of the Ru(bpy)$_3^{2+}$ probe, measured at 10% of peak height, was used to assess its ability to interact electrostatically with the hydride-modified fused-silica surface.[19,26,28] A 0.1 mM solution of the probe in the MOPS solution was used. Alternatively, a 1.0 mM amitryptiline solution was used as a probe for silanol-related interactions.

IR Spectra. A total of 200 sample scans referred to KBr was used to collect spectra at a resolution of 2 cm^{-1}. The 50% w/w silica particles in KBr were used as substrates.

NMR Spectra. Solid-state ^{29}Si cross polarization-magic angle spinning (CP-MAS) NMR measurements were performed on silica particles with a sample-spinning rate of 10 kHz, contact time of 5 ms, and delay times of 1 s. In total, 3 000−8 000 scans were acquired.

AFM Imaging. Fused-silica wafer samples were probed, in triplicate, in the intermittent noncontact mode with a 42 N/m force constant and 300 kHz resonance frequency. A scan size of 2 μm × 2 μm was used throughout.

Contact Angle Measurements. The contact angle of a water drop deposited on a hydride-modified silica wafer held horizontally serves as an indirectly measure of its surface hydrophobicity. The procedure for droplet deposition has been described elsewhere.[21] The drop was lit from behind, and its image was taken with the

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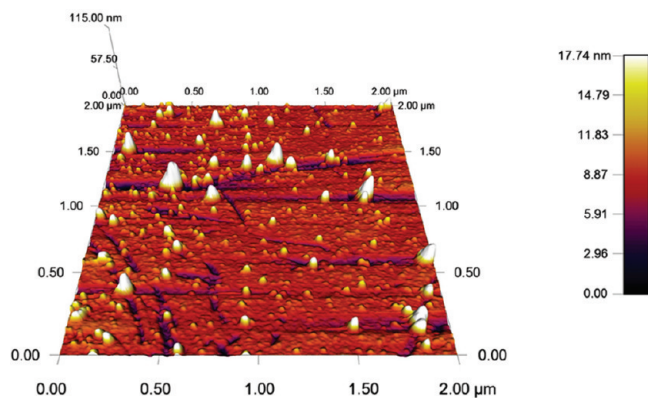(28) Fairbank, R. W. P.; Wirth, M. J. *Anal. Chem.* **1997**, *69*, 2258−2261.

Figure 1. AFM image of a silica wafer after hydride-modification according to a previous methodology.[3]

digital camera. Reported contact angles are the average of three measurements.

RESULTS AND DISCUSSION

Surface Modification. Unlike the new TES method, in the earlier approach (see reaction 2 above),[3] no dilution in a hydrocarbon is included and, as a result, the dioxane molecules compete very efficiently (via hydrogen-bonding) with the hydrolysate species for the reactive SiOH sites on the silica surface. At the high concentration of TES used in this approach, a strong bulk polymerization prevails and ultimately surface attachment of such molecular aggregates takes place. This is shown in Figure 1 for a silica wafer modified with TES in dioxane containing aqueous HCl, according to the former method. Notice the great extension of valleys (dark brown areas) between peaks. This blotched surface is consistent with the report of Pullen et al. on capillaries modified by the same method, where the spots the authors referred to as "hydride I" were attributed to unreacted silica.[12]

Compared to the former method, both new approaches produced a much more homogeneous coverage of the silica surface, as evidenced by AFM and shown in Figure 2. The success of the two new approaches was verified by diffuse reflection infrared Fourier transform (DRIFT) as well as ^{29}Si CP-MAS NMR, as depicted in Figures S-1 and S-2 for porous silica particles (see the Supporting Information). Briefly, the main feature of the DRIFT spectrum of the hydride is a strong Si−H stretching
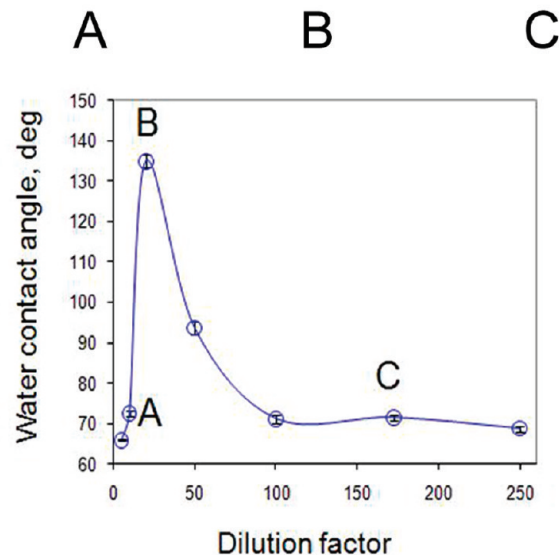

Figure 3. Effect of cyclohexane dilution of the TES-hydrolysate (50 mM TES, 0.15 M water, and 5.0 mM HCl in THF) on surface hydrophobicity, as measured by WCA. Hydrolysis and silane deposition times were 30 min each, at room temperature. Pictures on top of the graph show water microdrops on the hydride silica products marked with a letter on the curve. Error bars represent ±1 standard deviation ($n = 3$).

at about 2259 cm^{-1}. Similarly, ^{29}Si CP-MAS NMR spectra exhibit two characteristic peaks at about −84 and −74 ppm due to hydride-bearing silicon species. Both, IR and NMR, spectra of the new hydride substrates are indistinguishable from those of the conventional method. The new TES-method, though, appears to be much more desirable because the much lower reactivity and volatility of TES, compared to those of TCS, make it more easily manageable.

Hydrophobicity of Hydride Silica. The wettability of the hydride silica surface was assessed by measuring the water contact angle (WCA) on a wafer after silanization. The hydride silica made by both new methods showed significant hydropho-
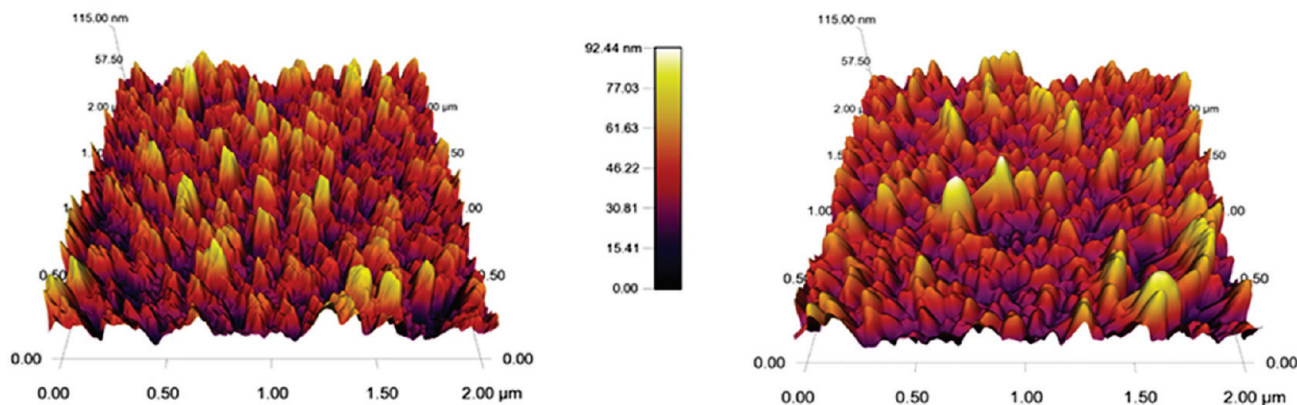

Figure 2. AFM images of silica wafers modified according to the new method utilizing TCS (left) and TES (right) silanizing agents. Reaction conditions were as described in the Experimental Section, except that a 20-fold dilution in cyclohexane was used in the TES-method.
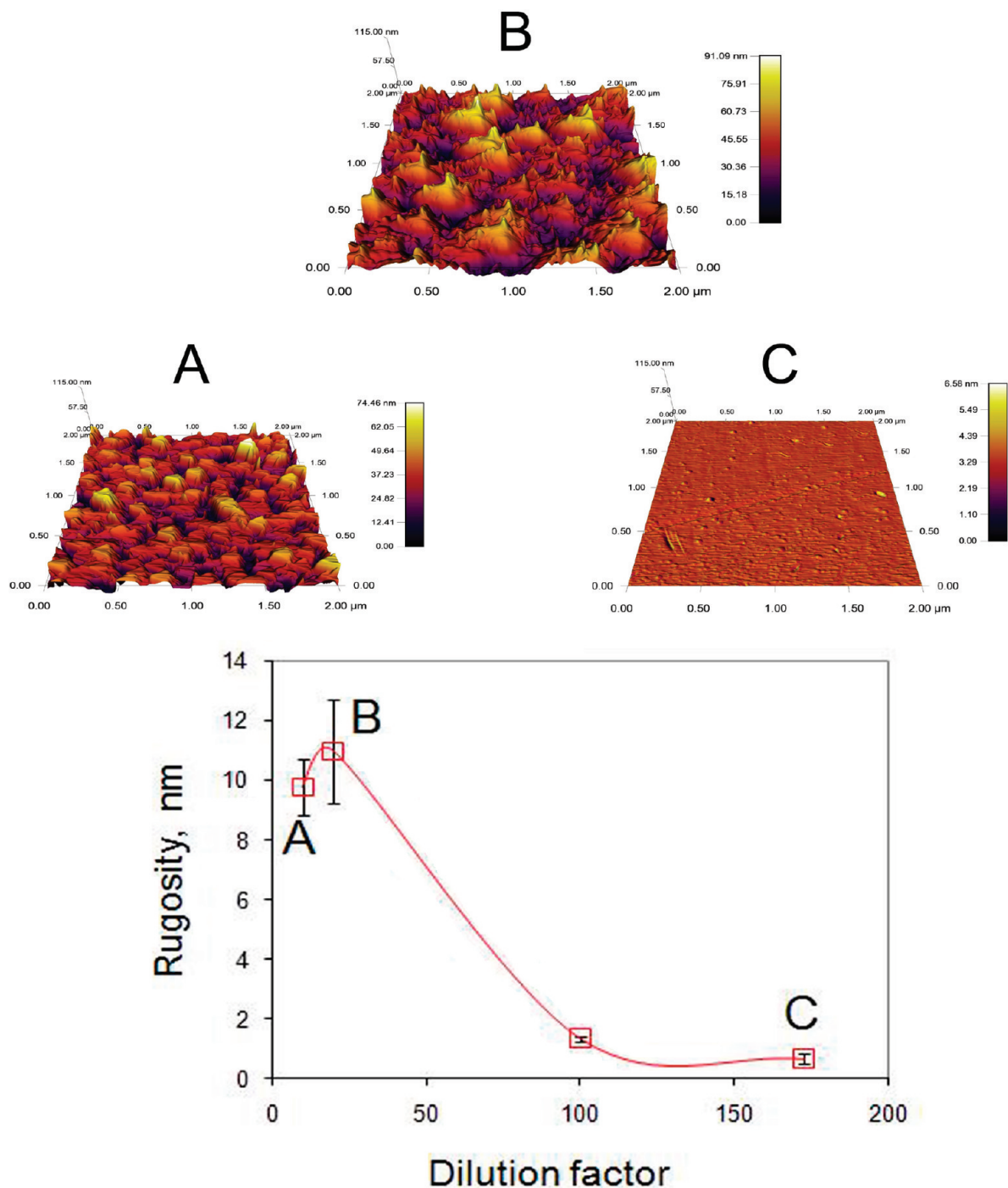
Figure 4. Effect of cyclohexane dilution of the TES-hydrolysate on surface roughness, as measured by AFM. Pictures on top of the graph show AFM images of the hydride silica products marked with a letter on the curve. Reaction conditions were the same as Figure 4. Error bars represent ±1 standard deviation (n = 3).

bicity, with typical WCAs of about 71° compared to 38° for the unmodified substrate and 57° for a wafer modified according to the former method. The higher hydrophobicity related to the native silica probably results from the lower polarity of the Si−H species compared to that of the Si−OH group. Of course, the presence of remaining silanols on the hydride silica (evidenced from DRIFT as well as ^{29}Si CP-MAS NMR spectra) may somewhat reduce its hydrophobic makeup. Also, a relatively lower hydrophobicity of the former method product is consistent with the patchy nature of the hydride silica surface (Figure

1). Clearly, this simple WCA test is very useful to rapidly and inexpensively obtain valuable information on the extent of surface modification (*vide infra*).

Controlling Polymerization during Silanization. While, as evidenced by AFM, the two new methods to make the hydride silica provide a surface uniformly covered with the anchored film, vertical profiles of the coatings (easily discernible in Figure 2) clearly indicate the formation of a multilayered film, which results from vertical polymerization of the silane (both, TCS and TES). In the present work, bonding of the SiH groups on the silica
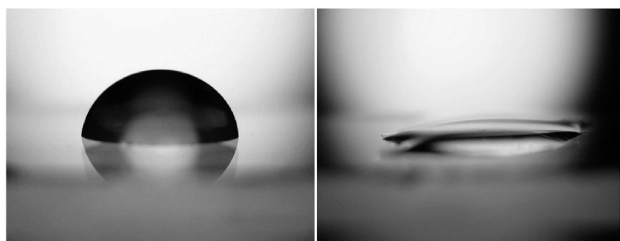
Figure 5. Photography of a water microdrop on the surface of a hydride-modified silica wafer before (left) and after (right) a 5 min exposure to a 25 mM MOPS buffer pH 7. Comparable results were obtained when the hydride-modified wafer was similarly exposed to deionized water, 0.1 M aqueous HCl, or 10% v/v water in THF.

substrate is done with chloride (TCS) and ethoxy (TES) precursors that undergo numerous hydrolysis and polycondensation reactions that result in the formation of polymers (sols) in solution. Upon contact with the silica, such polymers react with the surface silanols, forming the hydride substrate. If the sol particles grow beyond a certain desirable size and are then deposited on the silica surface, a rather rough surface such as those depicted in Figure 2 will result. In the TES-method, prior to bonding, the hydrolysate is drastically diluted in a nonpolar solvent (cyclohexane), which not only provides the driving force for the deposition to occur (as described above) but also maintains a relatively low concentration of the silane to prevent extensive polymerization. Dilution of the TES-hydrolysate in cyclohexane appears to be a critical experimental parameter that deserves further study. Figure 3 shows that a plot of WCA for a series of hydride-modified wafers as a function of the dilution factor of the hydrolysate in cyclohexane passes through a maximum, at a nearly superhydrophobic surface. Surface hydrophobicity is governed by both surface roughness and chemical composition. "Superhydrophobicity" is considered to be achieved when the WCA is greater than 150°.[29] Even though we have been able to obtain WCAs beyond this value, we have not attempted to optimize such property of the hydride. Notice that above a dilution factor of ~100 the WCA reaches a plateau. A similar plot of rugosity vs dilution (see Figure 4) not only follows the same trend, as expected, but also exhibits rugosity values at the plateau that approach that of a native silica wafer. Presumably, the hydride film is so thin that it essentially follows the contours of the unmodified substrate. Notice also that roughness as well as WCA values at the plateau exhibit a significantly better precision. It should also be pointed out that, under the experimental conditions used here, a dilution factor as high as 250 corresponds to an estimated TES/SiOH molar ratio of approximately 50, which still makes the hydride deposition very favorable. This is substantiated by a WCA of about 71° at the plateau of Figure 5, compared to approximately 38° for an unmodified silica wafer.

Hydrolytic Stability of the Hydride Silica. One expected effect of modifying a silica surface is a substantial decrease in the EOM of a CE tube. In a neutral electrolyte, essentially all silanols present on the inner wall of a fused-silica capillary are ionized and the remaining EOM at this pH might be utilized to indirectly assess the efficiency of a bonding reaction. Nonetheless, we found that a relatively short exposure of a hydride silica wafer to water (either as a neutral or acidic aqueous buffer or diluted
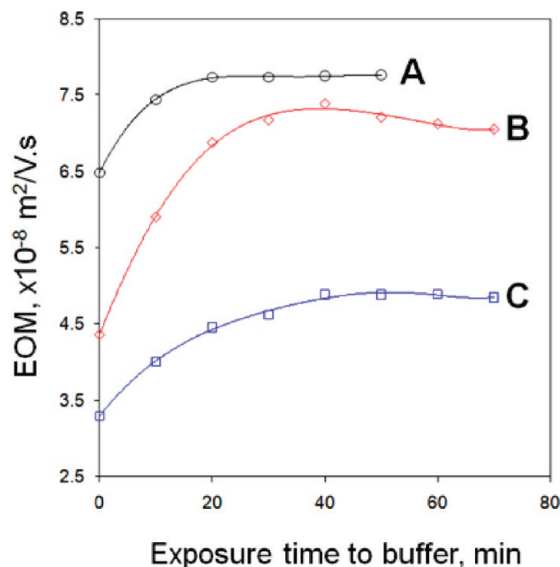

Figure 6. Effect of the time of exposure to 25 mM MOPS buffer pH 7 on the EOM of hydride-modified CE tubes. The buffer was forced through the capillary with 7 bar of N_2, which resulted in flow rates of 13−15 column volumes per min. Curve A corresponds to an unmodified capillary. Except for cyclohexane dilution factors (100- and 20-fold for curves B and C, respectively), capillary modification conditions were the same as Figure 4. CE conditions: L = 50.0 cm, l = 41.5 cm; hydrodynamic injection (3 s, 50 mbar); applied voltage, 10 kV (3.1 μA) for 3 min; 1 min buffer rinse between runs. Detection at 206 nm. Error bars ($\pm$1 standard deviation, n = 3), not shown, were smaller than the symbols used.

in an organic solvent such as THF) leads to a significant deterioration of its intrinsic hydrophobicity, as evidenced by a dramatic decrease in WCA (see Figure 5). The same behavior is seen in a wafer coated with a thin (dilution in cyclohexane ~100) or a thick (dilution ~20) hydride film. Since this observation strongly suggests a poor hydrolytic stability of the hydride silica, a parallel experiment was carried out with fused-silica capillaries to substantiate this finding. Figure 6 shows a plot of EOM vs time of exposure to a neutral buffer solution flowing through capillaries under pressure. Two capillaries were modified with thin and thick hydride films, respectively, while the third one was a native capillary included for comparison purposes. Evidently, all three capillaries exhibit a similar behavior: after an initially low value, the EOM increases until a plateau is reached. For the unmodified tube, this behavior is typical of its "conditioning" with the buffer solution.[26] In the case of the hydride tubes, after the first EOM measurement, the next 10 min of exposure to the neutral buffer (130−150 column volumes) are sufficient to completely hydrolyze the SiH groups, in good agreement with the observation depicted in Figure 5. Likely, subsequent exposure of the new SiOH-populated surface to the buffer resulted in its conditioning, just like a native capillary. Notice that while the capillary coated with a thin hydride film (curve B of Figure 6) reaches its plateau at an EOM level comparable to that of the native tube (curve A), the one coated with a polymeric layer (curve C) does so at a significantly lower level. This effect is most likely due to the greater roughness associated with the polymeric coating (see point B of Figure 4) compared to the flat surface that results from the thin hydride film. Naturally, this interpretation assumes that, under the same reaction conditions, the modification of a capillary tube

(29) Ma, M.; Hill, R. M. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 193–202.

Table 1. Typical Reaction Conditions for the Hydride-Modification of Three Different Silica Substrates by the New TES-Method

silica substrate	substrate dimensions	volume of diluted hydrolysate[a]	final TES concentration, mM	TES/SiOH molar ratio[b]	
				static[c]	dynamic[d]
wafer	25 mm × 9 mm × 1 mm	4.0 mL	0.5	125	
capillary	50 μm i.d. × 52 cm	1.0 μL	0.5	0.8	160
porous particles	1 g × 75.4 m^2/g	50 mL	16	1.25	

[a] Volume of reacting solution in contact with the silica surface at any given moment (one column volume in the case of the capillary). [b] Assumes a surface silanol concentration of 7.6 μmol/m^2 for native silica. [c] No pressure applied to the capillary. [d] 5.5 bar of nitrogen pressure applied, corresponding to about 10 column volumes/min for the capillary and hydrolysate used. The total amount of silane is calculated by taking into account the whole volume of silane solution that comes in contact with the inner capillary surface during the course of the reaction.

is similar to that of a wafer, something not difficult to accept. To further corroborate that the lower EOM was due to the greater roughness of the inner capillary wall and not to a surface partially populated with SiH species, an identical hydride-modified tube was exposed briefly (~1 min) to 0.1 M NaOH and then subjected to the same buffer conditioning process. The resulting EOM vs time curve (not shown) exhibited its plateau at essentially the same level as the lower curve in Figure 6. Since the NaOH solution rapidly and completely hydrolyzes all the SiH groups[3] and that it is assumed that no significant decrease of the surface roughness takes place during such short NaOH treatment, the EOM reaches the same level after conditioning with the buffer. Our observation had already been theoretically predicted by Hu et al.[30] and Quiao.[31] According to these researchers, when the thickness of the electric double layer is comparable to the surface roughness, the EOM becomes significantly reduced. Hu et al. estimated that the typical thickness of the electrical double layer associated with a 10^{-3} M KCl solution is about 9.6 nm,[30] a value that compares quite well with our rugosity measurement of about 11 nm corresponding to point B in Figure 4. Whereas Hu et al. and Quiao focused their work on microfluidic devices, to the best of our knowledge, this is the first time the effect of surface roughness on EOM is experimentally demonstrated in a typical CE tube.

In the early stages of this work, we attempted to indirectly monitor the effectiveness of the silanization process by evaluating the CE profile of certain compounds known to interact very strongly with remaining SiOH groups on modified silica surfaces. Such molecular probes included tris-2,2′-bipyridine ruthenium(II) chloride, as well as high pK_a compounds such as amitryptiline. It turned out that both probes, and very especially the Ru(II) compound, interacted so strongly with the buffer-exposed hydride silica that it was impossible to obtain reliable measurements of peak asymmetry or plate count from a capillary modified with a thick hydride coating. This observation is a further demonstration of the low hydrolytic stability of the hydride silica; the very poor peak shape strongly suggests an increased silanol population that results from the hydrolyzed SiH species and the roughed surface of the capillary.

Method Transfer from Wafers to Capillaries and Porous Particles. Because of their very high surface area (roughly 5 orders of magnitude larger than that for typical wafers and capillaries), porous silica particles require a significantly larger

amount of TES. Simple calculations involving typical reaction conditions for the different substrates used in this work reveal that transferring the surface-modification method from a wafer to a capillary tube by simply filling the later with the same reagent solution would result in a considerably lower TES/SiOH ratio, as shown in Table 1. Notice that, related to the capillary in the "static" mode (no pressure applied to move the liquid through the tube), the TES/SiOH ratio is about 2 orders of magnitude higher for the wafer. Thus, in order to increase such a molar ratio to a value comparable to that of the later, a flow rate of almost 20 capillary column volumes of the reacting solution per minute must be used. This is accomplished by a pressure difference of about 5.5 bar for the capillaries we used. The answer is not so straightforward in the case of porous silica particles. As seen in Table 1, a substantial increase of the concentration as well as the volume of the diluted hydrolysate provides only a modest molar excess of the silane (~25%). Naturally, the higher TES concentration required with porous silica imposes a rather low dilution factor in cyclohexane. Yet, assuming that the silane deposition is a very fast reaction, the dropwise addition of the diluted hydrolysate onto the silica suspension enables a further dilution. Cursory calculations show that an addition rate of two 15 μL drops per second over 30 min provides an effective dilution factor estimated between 35- and 300-fold as the reaction proceeds. Thus, the average dilution factor should be comparable to that for the impervious substrates. Of course, at the end of the reaction the deposition rate should decrease substantially, but a drastic dilution of the hydrolysate is effectively achieved and silane polymerization should be prevented.

CONCLUSIONS

A homogeneous (patch-free) thin hydride film can be formed on a silica surface by reaction with hydrolyzed TES from a dilute cyclohexane solution. This is an important improvement over the traditional methodology to prepare the silica hydride intermediate for surface bonding schemes based on the hydrosilylation reaction. Whereas the hydrolytic stability of hydride films deposited on impervious silica surfaces such as wafers and CE tubes is rather poor, this should not be a serious practical limitation since, in principle, the Si−H species will be eventually added to a terminal olefin (reaction 1) and thus converted to a stable Si−C linkage. While our finding appears to be contradictory to that of Pesek et al.[13,14,32] for hydride-based LC bonded phases, whether or not the

(30) Hu, Y.; Werner, C.; Li, D. *Anal. Chem.* **2003**, *75*, 5747–5758.
(31) Qiao, R. *Microfluid. Nanofluid.* **2007**, *3*, 33–38.

(32) Pesek, J. J.; Matyska, M. T. *J. Sep. Sci.* **2005**, *28*, 1845–1854.

limited stability of the hydride is shared by porous silica particles still needs to be demonstrated.

SUPPORTING INFORMATION AVAILABLE

IR and NMR spectral characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.