Organic Monolayers by B(C₆F₅)₃-Catalyzed Siloxanation of Oxidized Silicon Surfaces

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Supporting Information

ABSTRACT: Inspired by the homogeneous catalyst tris(pentafluorophenyl) borane [B(C₆F₅)₃], which acts as a promotor of Si–H bond activation, we developed and studied a method of modifying silicon oxide surfaces using hydrosilanes with B(C₆F₅)₃ as the catalyst. This dedihydrosiloxanation reaction yields complete surface coverage within 10 min at room temperature. Organic monolayers derived from hydrosilanes with varying carbon chain lengths (C₈–C₁₈) were prepared on oxidized Si(111) surfaces, and the thermal and hydrolytic stabilities of the obtained monolayers were investigated in acidic (pH 3) medium, basic (pH 11) medium, phosphate-buffered saline (PBS), and deionized water (neutral conditions) for up to 30 days. DFT calculations were carried out to gain insight into the mechanism, and the computational results support a mechanism involving silane activation with B(C₆F₅)₃. This catalyzed reaction path proceeds through a low-barrier-height transition state compared to the noncatalyzed reaction path.

INTRODUCTION

Surface functionalization of inorganic substrates such as silicon oxides (SiOₓ) and glass has been the focus of much attention and effort in the past few decades because of the potential applications of the functionalized materials in biomedicine, diagnostics and biosensing, surface chemistry, photonics, photovoltaics, and electronics. Among the different strategies for functionalizing silicon substrates, two approaches are frequently used. One is based on the attachment of organic self-assembled monolayers (SAMs), and the other is based on the deposition of multilayers or polymeric compounds. Although both approaches have significant potential, the attachment of SAMs is commonly preferred as it allows for the easy and highly controllable tuning of the surface properties and functionality.

The most common approaches used to prepare organic monolayers on silicon oxide surfaces involve the reaction between silanol groups (Si–OH) present on the oxidized silicon surface and functionalized organosilicon compounds, such as chlorosilanes, dimethylaminosilanes, alkoxysilanes, and allylsilanes, to form stable siloxane (Si–O–Si) bonds, although other methods for obtaining covalently bound organic monolayers are also increasingly being explored. Despite the simplicity of these approaches, uniform monolayers are difficult to obtain using solution-phase deposition methods, and undesirable polysiloxane networks are often formed. In addition, these surface modification approaches often require long reaction times, commonly taking 2–24 h. In silicon nanowires (SiNWs) can function as a specific example. SiNWs are quasi-one-dimensional structures with diameters of less than 100 nm, resulting in high surface-to-volume ratios. Because of these high ratios and their quasi-one-dimensional electronic structures, SiNW-based devices have properties that can outperform those of their traditional counterparts in many potential applications in the design of sensors, solar cells, Li-ion batteries, and superhydrophobic surfaces. Most modification processes for oxidized SiNW are based on silanization, esterification, and phosphonate attachment reactions, although hydroxylation in particular has been used heavily for oxide-free H-terminated SiNWs. Each of these functionalization approaches typically requires at least several hours (sometimes even

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Scheme 1. Schematic Representation of B(C₆F₅)₃-Catalyzed Grafting of Hydrosilane Derivatives (1−5) onto Oxidized Si(111) Surfaces
frequencies were calculated at this level, and the nature of the stationary points was determined. Initially, a Monte Carlo conformational search using the conformer distribution option available in Spartan 14 was used. With this option, a search without constraints was performed for every structure. The torsion angles were varied randomly, and the obtained structures were fully optimized using the MMFF force field. Thus, 100 minima of energy within an energy gap of 10 kcal·mol⁻¹ were generated. These structures were analyzed and ordered considering the relative energy, with the repeated geometries eliminated. In all cases, all conformers within 4.0 kcal·mol⁻¹ of the lowest-energy conformer were studied quantum chemically. The results refer to that conformer that displayed the lowest energy in the quantum chemical calculations.

## RESULTS AND DISCUSSION

### Monolayer Preparation
To study the grafting of hydrosilanes onto oxidized silicon surfaces catalyzed by the strongly Lewis acidic organoborane B(C₆F₅)₃ (Scheme 1), hydrosilanes bearing alkyl chains with different lengths [CH₃(CH₂)n—CH₂—Si(CH₃)₂—H, n = 6–16] were synthesized in high yields [Cs (1), C₁₀ (2), C₁₂ (3), and C₁₈ (4), Scheme 1] from the corresponding chloro(alkyl)dimethylsilanes by reduction with LiAlH₄, following a described procedure. All of these hydrosilanes showed an intense IR band centered at 2187 cm⁻¹ corresponding to Si–H stretching mode, a multiplet in the 1H NMR spectra at 3.70 ± 0.07 ppm and 13C NMR peaks between 12.4 and 5.0 ppm corresponding to Si—CH₃.

Initially, Si(111) samples were cleaned and oxidized by acetone sonication, plasma cleaning (10 min), and oxidation in piranha solution (H₂SO₄/H₂O₂ 3:1). Next, the reaction oxidized Si(111) and dimethyl(octyl) silane (1) in the presence of the boron catalyst was optimized using various conditions. All reactions were performed by immersing the freshly oxidized surface in a vial with 2 mL of dichloromethane solution containing 0.5 mmol of freshly oxidized surface in a vial with 2 mL of dichloromethane (0.27 and 0.28, respectively), indicating that the reaction was completed within 5 min. The samples reacted for 30 min (Table 1, entry 2) and 10 min (Table 1, entry 3) showed almost identical C/Si ratios (0.27 and 0.28, respectively), indicating that the reaction was completed within 5–10 min. Such grafting was also corroborated by an increase in the static water contact angle (SCA) from ~10°, due to the hydrophilic hydroxyl groups across the OH-terminated surface, to 103° and the formation of an organic monolayer with a thickness of ~0.8 nm as measured by ellipsometry and XPS (according to the C/Si ratio). Lowering the catalyst loading to 1% continued to give similar C/Si ratios (Table 1, entry 4). Finally, it is worth mentioning that reaction also occurred in the absence of solvent (Table 1, entry 5). No changes in the XPS spectra were observed upon rinsing and sonication with CH₂Cl₂, suggesting the formation of covalently bound monolayers. The use of another Lewis acid, such as BF₃, was also studied (5 mol %, CH₂Cl₂), however, no surface modification was observed when this catalyst was used.

Table 1 reports the XPS data, which revealed that the C/Si content increased notably relative to that of the unmodified substrate (Table 1, entry 1), indicating the effective grafting of the hydrosilane derivatives. Notably, both ellipsometry and XPS indicated the formation of a clean monolayer, without multilayer formation, as seen, for example, in the ellipsometry thickness values of about 0.86–0.91 nm and the XPS-inferred thickness (1.01 ± 0.20 nm for entry 5), in accordance with the expected thickness based on a fully stretched alkyl chain of this length (0.90 nm).

A detailed study of the reaction time showed that the reaction was complete after 5–10 min, as confirmed by the XPS analysis of the C 1s region of I-derivatized surfaces for different reaction times (Figure 1B). Reaction times were similar to those reported for the B(C₆F₅)₃-catalyzed hydrosilane modification of amorphous mesoporous silica micro-particles and hydroxyl-terminated porous silicon surfaces. Small bubbles of hydrogen gas were observed evolving from the solution during the grafting procedure, in line with the reaction being dehydrogenative. As shown, the reaction time for the B(C₆F₅)₃-catalyzed attachment of hydrosilane compounds to oxidized silicon (5–10 min) is far superior to those of typical silanization reactions (2–18 h).

### Monolayer Characterization
Next, to study the influence of the alkyl chain length on the formation of the monolayer, the attachment of hydrosilanes bearing chains of different lengths [CH₃(CH₂)n—CH₂—Si(CH₃)₂—H, n = 6–16] was studied under the optimized conditions [5 mol % B(C₆F₅)₃, 10 min]. Hydrosilane-modified silicon surfaces had SCAs between 103° and 111°, increasing with the hydrosilane chain length (Table 2). In particular, the SCA value for C₁₈-hydrosilane 4 of 111° corresponds to literature values reported for self-assembled monolayers of alkylsilanes on silicon oxide, indicating that the long-chain hydrosilane formed densely packed layers on the substrate surface.

As reported in Table 2, the ellipsometric thicknesses dₑlsps of the alkyl-terminated monolayers investigated in this study were found to be in accordance with those obtained by XPS (dₓps, using the C/Si ratio) and similar to the expected thicknesses calculated for densely packed monolayers with fully extended molecules and a near-perpendicular orientation to the surface. No evidence of the formation of multilayers was found by ellipsometry or XPS, indicating a clean surface modification reaction, especially when compared to other solution-based chemistry modifications on oxidized silicon substrates, which usually require longer reaction times.

Figure 2 shows the grazing-angle attenuated-total-reflectance infrared (GATR-IR) spectra of an ozone-oxidized Si surface and 1–4 hydrosilane-functionalized surfaces. Analysis of the CH₂ stretching vibrations of the prepared monolayers by GATR-IR spectroscopy revealed the absence of short-range ordering of the monolayers, as shown by the antisymmetric and symmetric C–H stretching vibrations at 2927 and 2856 cm⁻¹, respectively (see Supporting Information, Table S1).
This is attributed to the presence of Si-bound methyl groups. The hydrosilane-modified silicon surfaces also showed a clear CH$_3$ stretching vibration at 2965 cm$^{-1}$.

The topography of Si surfaces after the B(C$_6$F$_5$)$_3$-catalyzed modification was studied by atomic force microscopy (AFM). The root-mean-square (rms) roughness of the bare Si(111) substrate was found to be 0.42 nm, which decreased to 0.10 nm after piranha cleaning. After hydrosilane grafting, a uniformly coated surface was observed with a roughness of <0.3 nm for all surfaces (see Supporting Information, Table S2). No evidence of islands or granules was observed in the AFM images, in accordance with the presence of a fully formed monolayer on the surface.

Quantum Chemical Studies of Possible Mechanism. Whereas the B(C$_6$F$_5$)$_3$-catalyzed hydrosilylation of carbonyl compounds has been examined in detail both experimentally and theoretically, no computational studies on the catalytic activation of hydrosilanes and their novel reactions with oxidized silicon substrates have been performed. A mechanism for this grafting procedure based on previous reports on Si−H activation by borane compounds along the lines proposed by Nakanishi and Shimada involves the formation of a highly active intermediate by reaction of the B(C$_6$F$_5$)$_3$ catalyst with the hydrosilane (Figure 3A; intermediate I). The silicon atom in this intermediate is electron-deficient and therefore attacks the electron-rich silanol oxygen atom at the silica surface, which has acidic character (pK$_a$ = 4.9 − 8.5), to form an anionic species and a cationic intermediate (intermediate IV). Finally, the basic hydride intermediate abstracts a proton from silanol groups or the cationic intermediate, thereby regenerating the catalyst and yielding the immobilized product and hydrogen gas (as observed experimentally).

On the basis of this mechanism, we examined a model reaction system consisting of dimethyl(propyl)silane (6) and a glass model surface [Si(OH)$_4$] to reveal how the silane is activated by B(C$_6$F$_5$)$_3$. This reaction involved a high activation barrier of 44.8 kcal/mol, in agreement with the observation that no reaction was observed at room temperature in the absence of B(C$_6$F$_5$)$_3$. First, the noncatalyzed reaction was studied quantum mechanically by M11/6-311+G(d,p) calculations. (Cartesian coordinates of all stationary points as obtained at this level of theory are given in Supporting Information section 6.) This reaction involved a high activation barrier of 44.8 kcal/mol, in agreement with the observation that no reaction was observed at room temperature in the absence of B(C$_6$F$_5$)$_3$. Next, we examined the B(C$_6$F$_5$)$_3$-catalyzed reaction, assuming that this Lewis acid activates the hydrosilane and effects the formation of a complex between B(C$_6$F$_5$)$_3$ and hydrosilane molecule with a linear Si−H−B bond arrangement. In our case, the calculations showed the

Table 2. Characteristics of Monolayers Derived from B(C$_6$F$_5$)$_3$-Catalyzed Attachment of Compounds 1−4 onto Oxidized Si(111): Static Water Contact Angles, XPS Data, and Monolayer Thicknesses (monolayer thicknesses are given in nm)$^{a}$

| hydrosilane | SCA (deg) | C 1s (%) | C/Si ratio | $d_{\text{ellips}}$ | $d_{\text{XPS}}$ | $d_{\text{thest}}$ |
|------------|-----------|----------|------------|-----------------|---------------|-----------------|
| 1          | 103       | 15.5     | 0.29       | 0.91 ± 0.10     | 1.01 ± 0.20   | 0.90            |
| 2          | 106       | 15.9     | 0.30       | 1.12 ± 0.15     | 1.18 ± 0.20   | 1.11            |
| 3          | 108       | 16.2     | 0.32       | 1.38 ± 0.14     | 1.27 ± 0.15   | 1.33            |
| 4          | 111       | 25.4     | 0.54       | 1.97 ± 0.12     | 1.80 ± 0.21   | 1.98            |

*a* Using 5 mol % B(C$_6$F$_5$)$_3$ (10 min, room temperature). Each data point represents the average of five separately prepared monolayers. *b* Monolayer thickness as obtained by ellipsometry. *c* Monolayer thickness as obtained by XPS using the C/Si ratio. *d* Monolayer thickness as derived from Chem3D-estimated length of fully stretched chain.

Figure 1. (A) XPS survey scans of an unmodified oxidized silicon surface after plasma and piranha treatment (black) and after modification with 1 (red). (B) Comparison of the XPS C 1s region of 1-derivatized surfaces for different reaction times [1 mol % B(C$_6$F$_5$)$_3$].
formation of borane−hydrosilane adduct I with a calculated complexation free energy of 18.1 kcal/mol with respect to the reactants. As illustrated in Figure 3B, a relatively strong and near-linear Si⋯H⋯B interaction between B(C₆F₅)₃ and dimethyl(propyl)silane can be observed, with Si−H and B−H bond distances of 1.57 and 1.39 Å, respectively.

The next step in the process involves the approach of the electron-rich oxygen of a silanol from the oxidized silicon surface to the back side of the Si−H bond in the now electron-deficient Si atom of the borane−hydrosilane intermediate I to form reactant complex II. In this intermediate, the distance between the silicon from the hydrosilane and the silanol oxygen is still 2.58 Å, and the B−H distance has been shortened to 1.34 Å, whereas the Si−H distance has been lengthened to 1.62 Å. Further approach of the oxygen to the silicon atom gives rise to transition state TS involving a small barrier of 7.9 kcal/mol, with Si−H and B−H distances of 2.30 and 1.22 Å, respectively. In this TS structure, the Si−O distance was found to be 1.92 Å (Figure 3C). Finally, the TS can give the acidic and cationic intermediate III, which, after proton transfer and H₂ formation, forms the product and regenerates the B(C₆F₅)₃ catalyst.

**Thermal and Hydrolytic Stability.** The hydrolytic stability of the hydrosilane-derived monolayers was studied under standardized “continuous-flow” conditions in four different aqueous media [deionized water, PBS (pH 7.4), HCl solution of pH 3, and NaOH solution at pH 11]. After 1,

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**Figure 3.** (A) Proposed catalytic cycle and (B,C) optimized structures of (B) intermediate I and (C) transition state TS for the B(C₆F₅)₃-catalyzed dedihydrosiloxanation on oxidized silicon surfaces at the M11/6-311G+(d,p) level of theory. Bond lengths are given in angstroms.

**Figure 4.** Hydrolytic stability as followed by SCA monolayers derived from 1−4 on oxidized Si(111) in (A) deionized water, (B) neutral PBS (pH 7.4), (C) an acidic solution (pH 3), (D) a basic solution (pH 11), and (E) thermal stability under dry heating in air (130 °C). The reported values are the averages of five surfaces.
3, 7, and 30 days, samples were cleaned and sonicated in water, following a standardized procedure. The hydrolytic stability was followed by SCA measurements (Figure 4) and by carbon desorption rates, using the C/Si ratio from XPS survey scans; in each case, data were normalized to the value of the surface as obtained directly after modification. After immersion for 1 or 3 days in all four solutions, no major changes were observed in the SCA or in the carbon percentage as determined by XPS with respect to the starting situation. After immersion for 3 days in H$_2$O, PBS, and pH 3 solutions, the contact angle dropped slightly (2°−3°), and the XPS C/Si ratio decreased by ∼4%. Even after 7 days of immersion in neutral or acidic media, only minor changes were detected, whereas only in basic solutions was an SCA reduction of 7% observed, in line with the 6% reduction of the percentage C content as determined by XPS. In water (Figure 4A) and physiological PBS solution (Figure 4B), no significant decrease in SCA was observed after a week (about 4° decrease), and only after 30 days was a decrease of 6° measured for monolayers containing compounds 1, 2, and 3; this effect was even smaller for the longer-chain monolayer, with only a 4° decrease. These results show the high stability of the monolayers, which hardly suffered from any hydrolysis under the studied conditions.

Under acidic conditions (Figure 4C), the water SCA showed very little change after 7 days and remained high, on average, even after 30 days. Here, the effect of chain length was more pronounced, as a decrease of 8−10° was measured for monolayers containing hydrosilanes 1, 2, and 3 after 30 days. The XPS data also showed a significant reduction of the C signal in these functionalized surfaces after 30 days at pH 3. In contrast, 4-functionalized monolayers showed only a 5° decrease. These results are similar to those found for an octadecylsilane monolayer on glass and alkylphosphonic acid monolayers attached to stainless steel.

Finally, in contrast to the high stability shown in physiological solution (PBS buffer) and acidic media, the stability under basic conditions (pH 11) was found to be lower, especially for the shorter 1-functionalized monolayer (Figure 4D), with a decrease in contact angle of 6% (from 103° to 100°) after 1 day, in contrast to the decrease of 1−2% for the other monolayers under study. This lower stability was also observed as the study was prolonged along 3, 7, and 30 days, indicating the hydrolysis of the shortest monolayer under study, with a total decrease of about 18% (from 103° to 84°) after 30 days. For the rest of the monolayers, the SCA remained above 92° after 30 days at pH 11. In particular, for the 4-functionalized monolayers, a higher stability was found (SCA > 100°) when compared to that of the C$_{18}$ monolayers prepared with chlorosilanes, and the stability was at least as good as that obtained for extensively cured (up to 120 h at 80 °C) phosphonate-bound C$_{18}$ monolayers. These results clearly show the potential of this surface modification as reaction times are significantly shorter than those of other well-established surface modification strategies.

Finally, the thermal stability of the different monolayers was studied at 130 °C in air. As observed in Figure 4E, exposure to heat for 1 or 3 days caused a decrease of only a few degrees in the SCA. Only upon extended heating (30 days at 130 °C) was the SCA decreased by 18°, 13°, and 11° for surfaces modified with 1, 2, 3, and 4, respectively, with the value for the octadecyl layer still >100°. Such length dependence was not as clearly observed for O,Si−C−bound trichlorosilane-derived monolayers, in which the heating also could effect additional curing, which was, of course, absent here.

**Microcontact Printing.** Given the high reaction rates, hydrosilane attachment might be of significant interest for reactive microcontact printing. Therefore, we investigated the microcontact printing of hydrosilanes onto freshly oxidized silicon surfaces. A polydimethylsiloxane (PDMS) stamp with 10-mm pillar-like features was prepared by curing a commercially available PDMS prepolymer on a patterned master. The PDMS was next covered with a mixture of chlorosilanes and 1 mol % B(C$_6$F$_5$)$_3$ in dichloromethane and subsequently brought into contact with the oxidized silicon substrate for 30 s. After thorough cleaning of the substrate, the surface displayed a 10-μm sphere pattern in the AFM phase image, confirming successful transfer of the pattern, as shown in Figure 5A. The average thickness calculated by AFM corresponded to a monolayer of 2.2 ± 0.3 nm. When the shorter hydrosilane 5 was used, a thickness of 0.8 ± 0.2 nm was measured for this monolayer (Figure 5B). The short (30-s) reaction time required for the microcontact printing approach shows the potential of the hydrosilane attachment reaction to functionalize and pattern oxidized silicon surfaces.

**Silicon Nanowire Modification.** Given the importance of silicon nanowires in the design of sensors, solar cells, and...
superhydrophobic surfaces and the high reaction rates of hydrosilanes, which sharply reduce handling times, we extended this protocol to modify SiNWs. Toward this end, SiNWs were prepared on Si(111) surfaces by chemical vapor deposition of B₂H₆ and SiH₄ (B/Si atom ratio of 1:20000) as precursor gases and gold as a catalyst. For the surface modification, the SiNWs were initially cleaned with plasma and piranha solution to activate the surface Si–OH groups. After the reaction (5 min, room temperature) with a mixture of 4 and 1 mol % B(C₆F₅)₃, the SiNWs became highly hydrophobic. The SCA increased from an initial value of less than 10° to a final value of 145°. More interestingly, a superhydrophobic surface was obtained when a (perfluorooctyl)hydrosilane 5 (thus bearing a C₈F₁₇ chain) was used, with a final SCA of 170° (Figure 6C). The successful modification of SiNWs was further corroborated by XPS. After reaction with 5 (Figure 6B), clear increases in the percentages of C and F were observed, confirming the effective grafting of the fluorinated compound. The XPS F/C atomic ratio calculated as an average of three different fluorinated-modified surfaces was 1.40 ± 0.12, in excellent agreement with the theoretical value of 1.42. A detailed investigation of the XPS C 1s spectra confirmed the successful monolayer formation, as shown by peak deconvolution into different components corresponding to the carbon atoms having different environments. As shown in Figure 5D, the C 1s spectrum was deconvoluted into six peaks in line with the monolayer structure: the Si–CH₃ peak at 285.0 eV and peaks for −CH₂=Si, −CH₂−CH₃, −CF₂, −CF₂−CH₃, −CF₂−, and the terminal −CF₃ at 285.8, 286.7, 291.3, 292.0, and 294.4 eV, respectively.

This approach represents one of the fastest methods for functionalizing oxide-coated SiNWs, as most of the approaches based on silanization reactions typically require long reaction times (from 3 to 24 h). Consequently, this rapid functionalization might have a wide range of potential applications because of its speed and the use of a nonmetallic catalyst.

**CONCLUSIONS**

The formation of robust and covalently bound organic monolayers on oxidized silicon surfaces can be rapidly (5–10 min) achieved at room temperature through hydrosilane attachment as catalyzed by B(C₆F₅)₃. Hydrosilanes H–Si(CH₃)₂R with alkyl chains R containing from 8 to 18 carbon atoms form highly stable self-assembled monolayers, as evidenced by 30-day-long testing in various media. As a proof of concept, we applied this methodology to functionalize SiNWs, and superhydrophobic surfaces were rapidly obtained using fluorinated hydrosilanes. A quantum chemical study of the catalyzed reaction pathway showed that the B(C₆F₅)₃ catalyst coordinates to the hydrosilane to form a stable B···H–Si complex. This activated silane complex undergoes a backside attack from the surface-bound Si–OH group to form a Si–C–O–Si bond, which finally yields the immobilized product and hydrogen. The catalyst reduces the activation barrier from 45 to 18 kcal/mol, yielding hydrosilanes as mild yet highly reactive monolayer-forming agents.

### ASSOCIATED CONTENT

#### Supporting Information

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Experimental details regarding characterization of the synthesized hydrosilanes 1–5 by X-ray photoelectron spectroscopy (XPS), static water contact angle (SCA) measurements, atomic force microscopy (AFM), ellipsometry, and ¹H and ¹³C NMR spectroscopies. Cartesian coordinates of stationary points at the M11/6-311+G(d,p) level of theory (PDF)

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.
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