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Mild and Efficient Functionalization of Hydrogen-Terminated Si(111) via Sonochemical Activated Hydrosilylation

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Supporting Information

ABSTRACT: Efficient chemical functionalization of hydrogen-terminated Si(111) with simple and bifunctional 1-alkenes was achieved via novel sonochemical activated hydrosilylation, utilizing just a simple ultrasonic bath. It is an extremely mild method that allows the specific attachment of unprotected bifunctional alkenes such as undecenol, undecylenic acid, and even a heat/UV-sensitive alkene, bearing an activated leaving group (*N*-succinimidyl undecylenate), without suffering any degradation.

Silicon forms the basis for devices that are the core of computing and information technology.[1] Device feature size and chip density is being pushed toward fundamental limits to the use of silicon in these applications. Although there are roadblocks due to the fundamental limits of silicon during the rapid miniaturization of integrated circuits,[2] silicon has found allies in a bid to overcome those hurdles.[3] Since the introduction of organic monolayers tethered directly on oxide-free silicon,[4] the silicon surface has been opened up to the vast resources of organometallic chemistry,[5] where tailor-made functional molecules can be employed to impart a specific property to the device.[6] Specifically, the hydrosilylation of the hydrogen-terminated silicon surface with terminal olefins[7] creates an interfacial Si−C bond of high bond strength and low polarity which not only passivates the silicon surface but also creates an extremely stable and robust hybrid material.[8] Ultimately, surface functionalization expands the utility of silicon extensively as it enables the conjugation of various molecules of interest for a broad range of applications such as organic electronics, biosensing, and bioimaging.[9]

To date, there are quite a number of activation methods developed for the hydrosilylation reaction on the hydrogen-terminated silicon surface including the use of radical initiators, catalysts, and electrochemical, photochemical, thermal, or microwave activation methods.[10] The selection of the most appropriate activation method largely depends on the type of silicon material, the target molecule, and the intended application. For example, the mild white light photochemical activation[11] is sought after for the direct attachment and photopatterning of labile biomolecules on flat silicon surfaces for the creation of a biosensor array. However, such mild activation methods often require long hours of reaction (>15 h) for complete functionalization, which inevitably increases the chance of surface oxidation. The use of ultrasound ranges from the basic cleaning of materials to the unique synthesis of nanostructured materials and the complex sonoluminescence process which all occur because of the extraordinary effect of acoustic cavitation.[12] Similarly, there are numerous reports of rate enhancement in a sonochemical assisted reaction including the sonochemical assisted hydrosilylation of organosilicon compounds and hydrogen-terminated silicon nanoparticles in the presence of expensive platinum catalysts.[13] In our present work, we discovered that the acoustic cavitation alone is capable of efficiently activating the hydrogen-terminated silicon surface for the hydrosilylation reaction with various terminal alkenes.

The sonochemical functionalization proceeds efficiently with just the use of a basic ultrasonic bath at room temperature and in the absence of a catalyst or radical initiator. By using octadecene as the classic example for functionalization of Si(111), its sonochemical activated attachment kinetics was determined by monitoring the thickness of the monolayer at different reaction times (Figure 1). It took just 1 h to form a self-limiting ideal monolayer thickness on *p*-type Si(111) which is of the same time frame as the UV photochemical activation method.[14] It is noteworthy that the efficiency and even selectivity of sonochemical reactions[15] can be further optimized depending on many experimental parameters (temperature, pressure, acoustic frequency, and intensity), properties of reaction mediums, and even the geometry of reaction vessels.[16] Nevertheless, the sonochemical functionalization carried out here proceeded rapidly in our current basic experimental setup and self-terminated upon formation of a complete monolayer as evident by the constant thickness even after extended (2 h) sonication. In contrast, three-dimensional growth of olefins on diamond was observed with extended illumination by using UV photochemical functionalization owing to side reactions[17] induced by the photoemission process.[18] The exact mechanism of sonochemical activation is currently unclear given the fact that acoustic cavitation can generate localized "hot spots" of extreme pressure, temperature, and even sonoluminescence which may induce various activated synthons such as the surface silyl radicals and excitons. Furthermore, the cavitation which occurs near an extended solid surface is nonspherical and drives high-speed jets of liquid into the surface which may constitute a mechanochemical effect. However, the propagation step is of radical nature, as predicted by calculation,[19] which explains the rapid functionalization. In brief, after the formation of the Si−C bond and the generation of a secondary alkyl radical on the alkene, the carbon radical then preferentially abstracts a hydrogen atom from a vicinal surface Si−H bond, thus creating a new surface silyl radical for subsequent attachment (Figure 1b).

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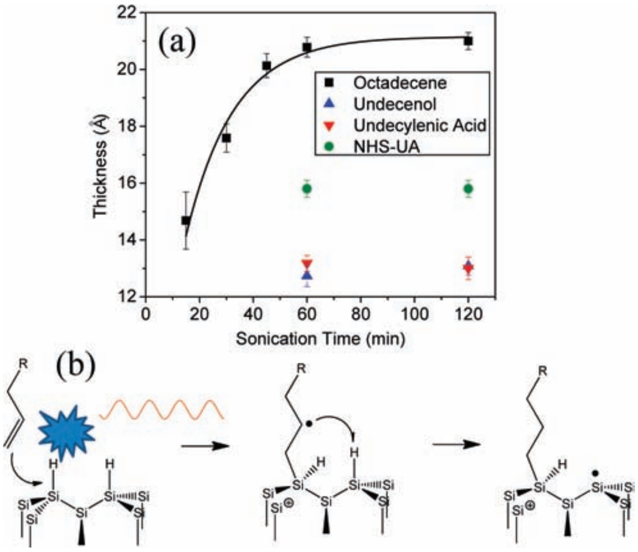

Figure 1. (a) Thickness of octadecene (■), undecenol (▲), undecylenic acid (▼), and *N*-succinimidyl undecylenate (NHS-UA, ●) functionalized Si(111) at various sonication times as measured via ellipsometry. (b) Mechanism of sonochemical activation of H-terminated Si(111) surface for hydrosilylation reaction with terminal alkene followed by radical propagation on the silicon surface.

Table 1. Water Contact Angle and Optical Thickness Measured by Ellipsometry of Functionalized Si(111) Samples before and after Immersion in Fluoride Solution at Room Temperature for 1 h

Samples	Contact Angle/deg	Thickness/Å
(i) Octadecene	111	21.0
-After soaking	111	21.1
(ii) Undecenol	67	13.1
-After soaking	66	13.2
(iii) Undecylenic Acid	43	13.0
-After soaking	42	13.0
(iv) NHS-UA	52	15.8
-After soaking	51	15.5

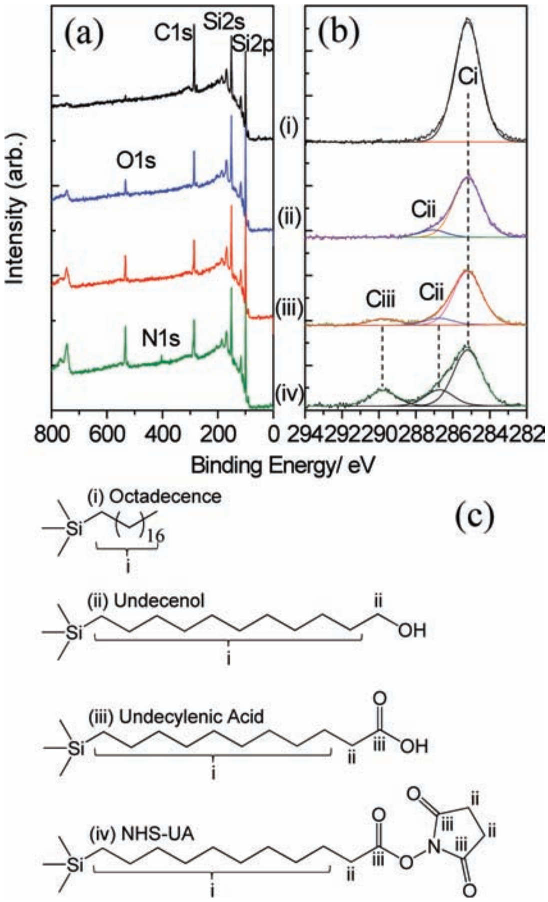

Figure 2. (a) XPS survey scans, (b) C1s XPS spectra, and (c) molecular structures of (i) octadecene, (ii) undecenol, (iii) undecylenic acid, and (iv) *N*-succinimidyl undecylenate (NHS-UA) functionalized Si(111).

Direct modification of the silicon surface with ω-functionalized 1-alkenes is highly sought after to directly impart functional groups without having to go through detrimental multistep reactions of protection and deprotection of the functional groups.[20] The application of the sonochemical functionalization was extended to bifunctional alkenes with a terminal alcohol (undecenol), carboxylic acid (undecylenic acid), and an activated ester (*N*-succinimidyl undecylenate, NHS-UA) which is prone to hydrolysis upon heat or UV activation. They were found to form complete monolayers of ideal thicknesses in 1 h which persisted even after extended sonication (Figure 1). This demonstrates that the sonochemical activation is mild but yet efficient. The water contact angles on undecenol, undecylenic acid, and *N*-succinimidyl undecylenate (NHS-UA) functionalized Si(111) were hydrophilic in contrast to that of the octadecene functionalization sample, indicating distinct differences in the terminal groups of the monolayers (Table 1). The water contact angle for NHS-UA functionalized Si(111) via sonochemical activation (52°) was similar to that formed via mild visible light, and remarkably, the undecylenic acid functionalized sample via the sonochemical activation (44°) was significantly lower than that obtained using the harsh UV photochemical activation (>50°).[21] This implies that more hydrophilic carboxylic acid groups were exposed on the monolayer surface which may be due to the structural ordering of the monolayer imparted by the mild sonochemical activation. A test of the monolayer stability was performed by immersing the samples in fluoride solution (48% HF/dioxane 1:9, v/v) at room temperature for 1 h, and it is apparent that all the monolayers remained intact as a result of strong interfacial Si−C bonding.

Elemental surface characterization was performed with X-ray photoemission spectroscopy (XPS) in which the survey scans show only the presence of expected elements for respective samples without any other elemental contaminant (Figure 2a). Also, the absence of oxidized silicon for all samples (see Supporting Information) indicates the formation of oxide-free functionalized surfaces. From the C1s XPS spectra (Figure 2b), a major peak at 285.2 eV (Ci), attributed to the long aliphatic carbon chain, could be fitted for all the samples. The peak shoulders (Cii) are attributed to the alcohol carbon (at 287.0 eV) for undecenol functionalized Si(111) or the α-carbons adjacent to the carbonyl carbon atoms (at 286.7 eV) for undecylenic acid

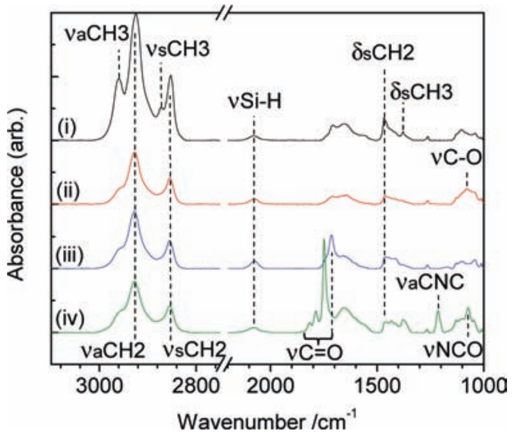

Figure 3. ATR-FTIR spectra of (i) octadecene, (ii) undecenol, (iii) undecylenic acid, and (iv) *N*-succinimidyl undecylenate (NHS-UA) functionalized Si(111) obtained using air as the background reference.

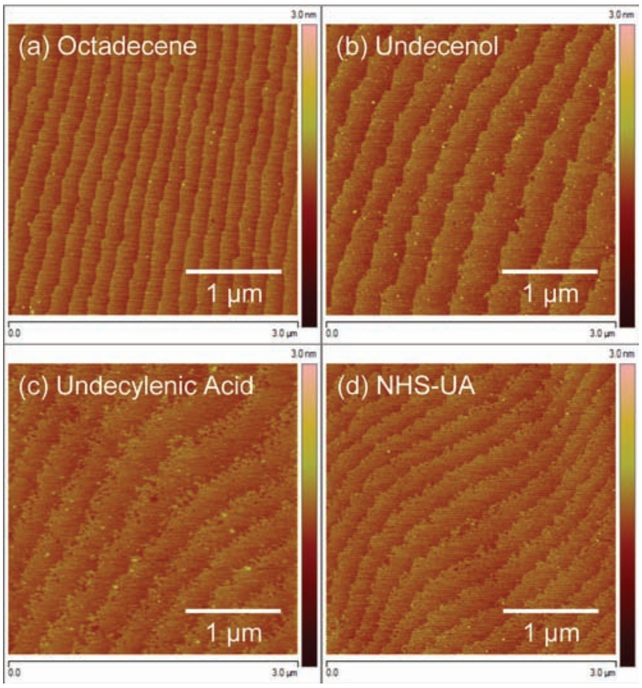

Figure 4. TM-AFM images of (a) octadecene, (b) undecenol, (c) undecylenic acid, and (d) *N*-succinimidyl undecylenate (NHS-UA) functionalized Si(111). Data height scale is 3 nm for all.

and NHS-UA functionalized Si(111). The distinctly shifted peaks at 289.8 eV (Ciii) are attributed to the carbonyl carbon as shown in the schematic depiction of the types of carbon atoms that are distinguishable by XPS (Figure 3c). The atomic ratio of the carbon components (see Supporting Information) of NHS-UA functionalized Si(111) via sonochemical activation (9.4:2.7:2.6) was close to the theoretical ratio and similar to that formed via mild visible light.[21] The aliphatic carbon components of undecenol and undecylenic acid functionalized Si(111) were slightly less than expected, as the photoelectrons from the lower aliphatic carbon chains were attenuated more due to their capability of forming a closer packed monolayer owing to their smaller head groups.

Qualitative surface analysis was carried out by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy to probe the vibrational features of the sample surface. All the functionalized Si(111) surfaces showed a small broad peak at 2080 cm^{-1} (Figure 3), attributed to residual unreacted Si−H after SAM formation.[22] The absence of a distinct peak at 1098 cm^{-1} for all samples indicates the absence of the Si−OR bond, and there is no sign of C═C stretching (1640 cm^{-1}) or ═CH_2 stretching (3050 cm^{-1}) which would otherwise be an indication of a side reaction.[23] It is clear that only the octadecene functionalized sample exhibits CH_3 stretching at 2961 cm^{-1} (asymmetric) or 2872 cm^{-1} (symmetric) and CH_3 deformation at around 1376 cm^{-1}, owing to its methyl end group. For the undecenol functionalized Si(111), the absorption peak due to C−O stretching at 1078 cm^{-1} shows the presence of the alcohol functional group,[24] whereas the sharp peak at 1713 cm^{-1}, attributed to C═O stretching, is an unambiguous indication of a free carboxylic acid group for the undecylenic acid functionalized sample.[25] For the NHS-UA functionalized Si(111), the appearance of the characteristic C═O stretching vibrations at 1817, 1788, and 1748 cm^{-1} belong to the ester carbonyl stretch and the symmetric and asymmetric carbonyl stretches in the succinimidyl end groups, respectively. Additionally, the peaks at 1214 cm^{-1} (asymmetric C−N−C stretch) and 1073 cm^{-1} (N−C−O stretch) also arise from the succinimidyl end group.[26]

Tapping mode atomic force microscopy (TM-AFM) images (Figure 4) of the four functionalized Si(111) surfaces exhibit topographies that were identical to that of the hydrogen-terminated Si(111) surface with atomically smooth terraces separated by atomic steps of 0.3 nm. The arithmetic mean of surface roughness (*Ra*) of 0.1 nm[27] was observed. This illustrates that the mild sonochemical activation method did not cause any damage to the substrate or organic monolayer and the compact and homogeneous monolayers conform to the atomically flat terraces of the Si(111) surface.

In conclusion, we have demonstrated the use of a simple ultrasonic bath for activation of the hydrogen-terminated Si(111) surface for hydrosilylation with various terminal alkenes. This novel sonochemical functionalization method is efficient but yet mild enough for direct attachment of bifunctional and heat/UV sensitive alkenes. For future work, the sonochemical approach may very well be extended to functionalization with other classes of organics such as alkynes or other forms of hydrogen-terminated silicon substrates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures and table of atomic ratio of the carbon components. This material is available free of charge via the Internet at http://pubs.acs.org.

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