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## Surface Chemistry

# Radical-Induced Hydrosilylation Reactions for the Functionalization of Two-Dimensional Hydride Terminated Silicon Nanosheets

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**Abstract:** Herein we present the functionalization of freestanding silicon nanosheets (SiNSs) by radical-induced hydrosilylation reactions. An efficient hydrosilylation of Si–H terminated SiNSs can be achieved by thermal initiation or the addition of diazonium salts with a variety of alkene or alkyne derivatives. The radical-induced hydrosilylation is applicable for a wide variety of substrates with different functionalities, improving the stability and dispersibility of the functional SiNSs in organic solvents and potentially opening up new fields of application for these hybrid materials.

Silicon nanosheets (SiNSs) are two-dimensional semiconducting materials with a layer thickness in the nano-regime and sheet sizes up to the micro-scale.[1] Like graphene they combine outstanding structural and electronic characteristics. As the electronic properties of these two materials differ from each other, SiNSs should hence expand the field of applications for 2D nanomaterials.

According to theoretical and experimental studies the band gap of SiNSs is tunable by physical strain,[2] the degree of hydrogenation, termination with heteroatoms,[3,4] and surface functionalization with different substrates.[5,6] Additionally, SiNSs exhibit unique optical properties such as a layer-thickness-dependent absorption edge[7] and photoluminescence (PL) emission arising from an enhanced direct band gap transition.[8,9] Hence SiNSs are promising candidates for microelectronics such as novel field effect transistors (FET)[5,10] and photovoltaic solar cells[9] and have already been proven to exhibit potential for lithium ion battery application.[11–13]

Several routes have been reported for the production of SiNSs. They can be synthesized by magnesiothermic reduction of $SiO_2$[14,15] or grown on supports such as Ag and Si by chemical vapor deposition.[8,16,17] Another straightforward and easily scalable route is chemical exfoliation from $CaSi_2$.[18,19] The Zintl salt $CaSi_2$ consists of interconnected $Si_6$ rings which form puckered two dimensional, anionic silicon sheets and planar monolayers of $Ca^{2+}$ ions. Through treatment with hydrochloric acid the $Ca^{2+}$ ions can be deintercalated giving exfoliated hydride terminated SiNSs (Figure 1).

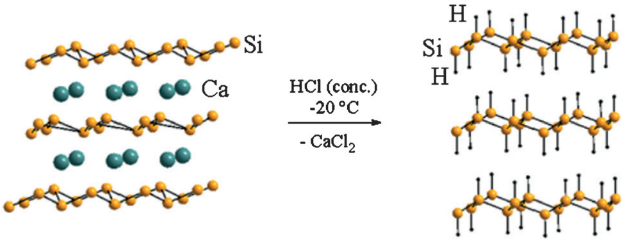

**Figure 1.** Synthesis of layered polysilanes by chemical exfoliation from $CaSi_2$.

Due to their structural properties (i.e., $sp^3$ character), hydride terminated SiNSs are also referred to as layered polysilanes.[20] They are prone to oxidation under ambient conditions and must therefore be functionalized to be of further use. Additionally functionalization breaks up the stacked structure of non-functionalized SiNSs, rendering freestanding monolayers. Functionalized SiNSs are dispersible in organic solvents which facilitates their handling and characterization.

So far only three different methods have been published in which the functionalization of hydride terminated SiNSs with organic compounds is described. The reaction with *n*-alkylamines leads to stable Si–N–Si derivatives which exhibit blue PL,[21,22] while the conversion of SiNSs with the Grignard compound PhMgBr renders $(Si_6H_4Ph_2)_n$ layers.[1] Additionally Pt-catalyzed hydrosilylation with 1-hexene enables the functionalization of SiNSs and yields stable colloidal dispersions in chloroform.[23]

Hydrosilylation reactions can be used to react molecular and surface Si–H groups with various unsaturated substrates. The reaction does not take place spontaneously, but needs initia-

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tion. On the molecular level it can be mediated by a catalyst, while on surfaces, thermally or initiator-induced radical reactions are also possible.[24–26] The latter are easily feasible, cost-efficient and tolerant towards a broad variety of functional groups. Another advantage is that radical-induced hydrosilylation is conducted without the introduction of transition metal impurities which are known to alter the PL properties of silicon nanomaterials[27,28] and lead to increased surface oxidation.[29] Despite their advantages, radical-induced hydrosilylation reactions have not yet been examined for the surface functionalization of SiNSs.

In this work the reactivity of SiNSs towards unsaturated compounds with different functionalities was examined (Scheme 1). The reactions were conducted in the absence of a catalyst under thermal initiation (130 °C) or by the addition of a diazonium salt as radical initiators with a variety of functional substrates. The resulting hybrid materials were fully characterized by FTIR, NMR spectroscopy, AFM, TGA, XRD and PL measurements.

The hydride-terminated SiNSs used in this work were synthesized following a literature known procedure.[19] $CaSi_2$ was chemically exfoliated with HCl (conc.) at −20 °C for 7 days. To remove residual oxide the obtained SiNSs were then etched with hydrofluoric acid and extracted with dichloromethane. As can be seen from the Si–H stretching- (≈2100 $cm^{-1}$), scissoring- (≈900 $cm^{-1}$) and wagging bands (≈860 $cm^{-1}$) in FTIR spectra of the freshly etched SiNSs, the resulting silicon sheets are hydride-terminated with only slight traces of Si–O (≈1100 $cm^{-1}$) and no Si–OH (Figure 2 a).

To understand the reactivity of the SiNSs towards unsaturated carbon compounds, control experiments were conducted without a radical initiator at room temperature in the dark. Therefore the HF treated SiNSs (15 mg) were dispersed in a mixture of dry toluene (2 mL) and 1-dodecene (3 mmol), degassed by three freeze-thaw-pump cycles and subsequently stirred overnight under argon in the dark.

Neither molecular silanes[30,31] (see the Supporting Information) nor hydride terminated silicon surfaces of bulk silicon[32] or nanostructured silicon[33] show functionalization under these conditions. Therefore we were surprised to observe a significant amount of dodecyl groups on the SiNSs in FTIR measurements (Figure 2 c) and TGA (Figure S7 in the Supporting Information). However this functionalization method is not sufficient to fully prevent stacking of the SiNSs (Figure S8 in the Supporting Information). Additionally, after the workup strong Si–O and residual Si–H bands, visible in IR spectra indicate, that the functionalization only takes place to a minor extent.

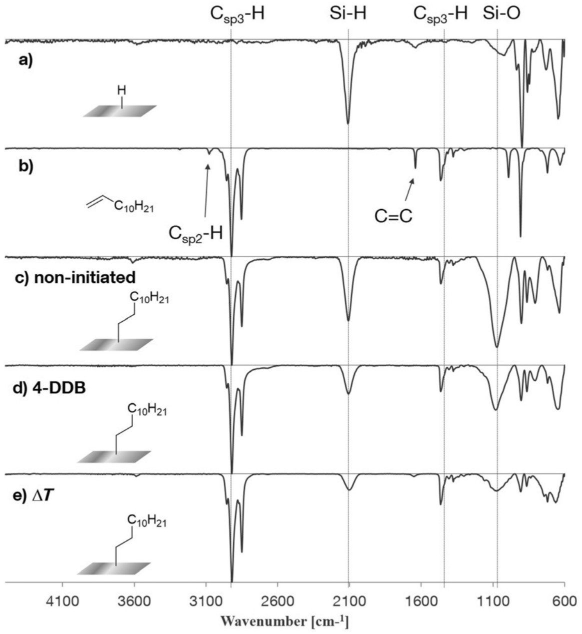
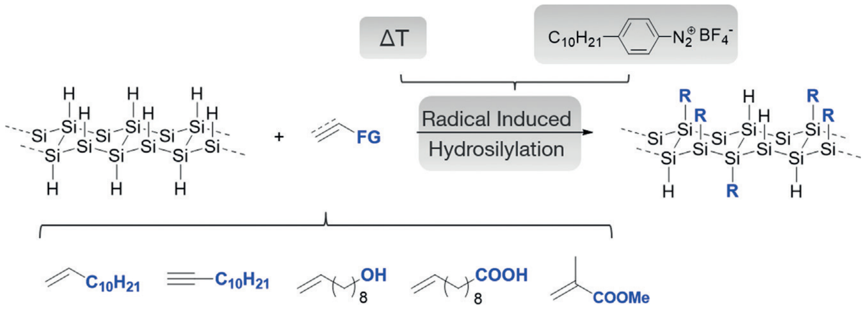


**Figure 2.** FTIR spectra of: a) freshly etched SiNSs, b) 1-dodecene and 1-dodecene-functionalized SiNSs, c) without the addition of an initiator, d) with 4-DDB, and e) Δ*T*-induced hydrosilylation.

The cause for this unprecedented reactivity is not fully understood and remains part of the ongoing research in our group. Potential explanations are the very high surface area and energy which results in a higher reactivity of the nanomaterial[34] or the surface activation by traces of oxygen which were shown to initiate hydrosilylations on SiNCs.[35]

To achieve a higher degree of surface functionalization, the SiNSs were subsequently treated with 1-dodecene under radical initiation conditions (Scheme 1).

Diazonium salts are known to be mild radical initiators for hydrosilylation reactions on nanostructured silicon.[36] Especially 4-decylbenzene diazonium tetrafluoroborate (4-DDB) is suitable due to its solubility in nonpolar solvents.[26] Additionally elevated temperatures can initiate hydrosilylation.[35]



**Scheme 1.** Schematic overview of the executed functionalization methods: Thermal and diazonium salt induced hydrosilylations are applicable on a broad variety of substrates.

Exfoliated SiNSs (15 mg) were etched with HF (48 %), extracted and dispersed in a mixture of dry toluene (2 mL) with 1-dodecene (3 mmol). After degassing, 4-DDB (15 μmol) was added and the reaction mixture was stirred at room temperature, overnight. For thermal functionalization Si–H-terminated SiNSs were dispersed in 1-dodecene (1 mL), degassed and subsequently stirred at 130 °C, overnight.

The mechanism for both initiation conditions is proposed to proceed by the formation of silyl-radicals.[37] The 4-DDB-induced functionalization occurs through reduction of the diazonium compound, release of nitrogen and hence the formation of an aryl radical. After deprotonation a silyl surface radical is formed which then reacts with the unsaturated compound, leading to the Si–C bond and a carbon centered radical. Abstraction of a neighboring hydrogen radical again forms a silicon surface radical and the hydrosilylation proceeds as a radical chain reaction (Scheme 2 a).[26,38]

Thermally induced hydrosilylation is stated to be dependent on the reaction temperature. While temperatures ≥150 °C provide enough energy to homolytically cleave Si–H bonds and thus induce the radical chain propagation (Scheme 2 b), for temperatures between 80–150 °C traces of oxygen are proposed to accelerate hydrogen abstraction (Scheme 2 c).[35]

After the reaction, the FTIR spectra of the functionalized SiNSs (Figure 2 d and e) show strong $C_{sp3}$–H bands ($\approx$2920 cm$^{-1}$, $\approx$1460 cm$^{-1}$) while only weak bands of residual Si–H ($\approx$2100 cm$^{-1}$) and Si–O ($\approx$1100 cm$^{-1}$) are present. This indicates a higher coverage of the SiNSs with dodecyl groups in contrast to functionalization without radical initiation, which is also supported by differences in the weight loss of the differently functionalized material in TGA measurements (Figure S7 in the Supporting Information).

Additionally we confirmed the 4-DDB and thermally induced functionalization with $^1$H NMR experiments in solution (Figure 3). Due to the restricted freedom of movement of the organic substrates attached to the Si surface the spectra can only qualitatively be used to show the successful functionalization and purification. The peaks of the double bond (A: $\delta=5.82$ ppm; B+C: $\delta=4.96$ ppm) and the methylene group next to it (D: $\delta=2.04$ ppm) have vanished and the spectra still show the peaks of the terminal $CH_3$ group (F: $\delta=0.85$ ppm) and of the –$CH_2$ groups (E: $\delta=1.25$ ppm) of the alkyl chain.

Atomic force microscope (AFM) images of the 1-dodecene-functionalized SiNSs show freestanding monolayers with a thickness of about 2.0 nm (Figure 4) which is similar to the

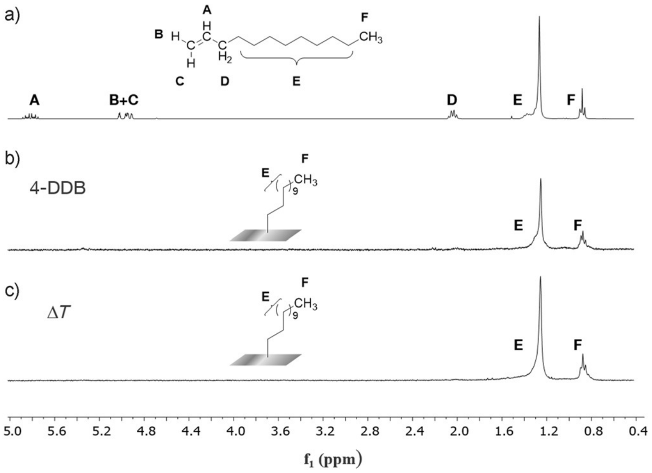
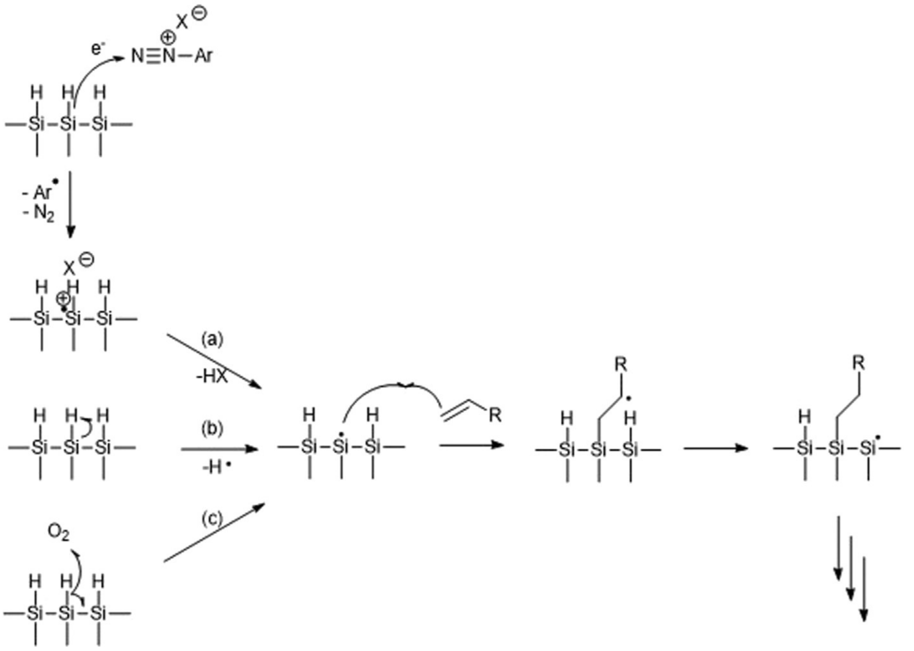


**Figure 3.** NMR spectra of: a) 1-dodecene, 1-dodecene-functionalized SiNSs with b) 4-DDB, and c) Δ*T*-induced hydrosilylation.



**Scheme 2.** Proposed mechanism for the: a) diazonium-compound induced mechanism and thermally induced hydrosilylation at temperatures between b) 80–150 °C, and c) ≥150 °C.[25,35,39]

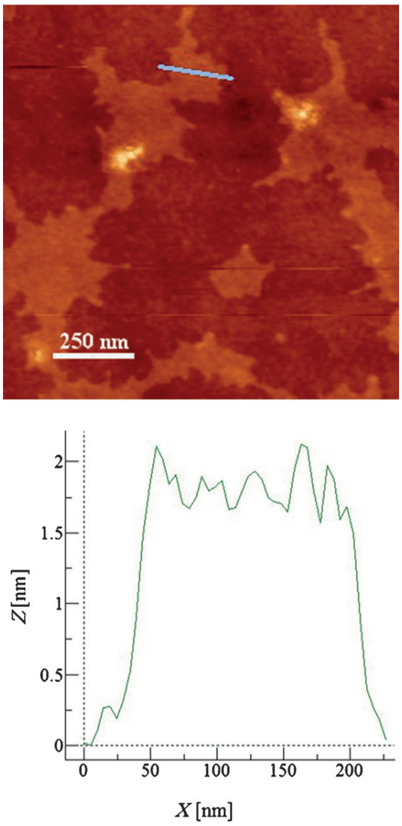


**Figure 4.** Non-contact mode AFM image of 4-DDB-induced 1-dodecene-functionalized SiNSs (top) and their line profile (bottom) taken along the line in the left image.

thickness of the 1-hexene-functionalized SiNSs reported by Nakano et al.[23]

XRD patterns recorded from the non-functionalized and 1-dodecene-functionalized SiNSs show that the characteristic reflections of the stacked, non-functionalized sheets decrease significantly in intensity when the SiNSs are functionalized without the initiator and even further with radical initiation (Figure S8 in the Supporting Information). The long dodecyl chains on the surface seem to stabilize the monolayers and hinder the SiNSs from stacking, resulting in a less ordered material.

Besides the model substrate 1-dodecene, functional substrates are promising candidates for further applications of the hybrid nanomaterials. Hence, to demonstrate the broad applicability of thermally and diazonium salt-induced hydrosilylations with hydride terminated SiNSs, a number of functional alkenes and alkynes were used. In this context we explored the functionalization with 10-undecenoic acid, 1-dodecyne, 9-decen-1-ol and *tert*-butyl methacrylate (*t*BuMA). In the case of *t*BuMA thermal hydrosilylation leads to a vast excess of polymerized alkene. No such side reaction could be observed in the 4-DDB-induced functionalization of the SiNSs, demonstrating the advantage of this mild method.

FTIR spectra of the functionalized SiNSs (4-DDB: Figure 5; Δ*T*: Figure S9 in the Supporting Information) with the different substrates confirm the successful reaction exhibiting the expected bands such as $C_{sp3}$–H (≈2920 $cm^{-1}$), C=C (≈1640 $cm^{-1}$), C=O (≈1700 $cm^{-1}$), OH (≈2920 $cm^{-1}$), C–O (≈1150 $cm^{-1}$) while only traces of Si–H (≈2100 $cm^{-1}$), and Si–O (≈1100 $cm^{-1}$) can be detected. SiNS–$C_{10}H_{20}OH$ and SiNS–$C_{10}H_{20}COOH$ are dispersible in protic solvents such as ethanol and methanol while for SiNS–$C_{12}H_{25}$ and SiNS–CHCH–$C_{10}H_{21}$ nonpolar hydrocarbons such as toluene and benzene are the solvents of choice. Further reactions are possible with the thus introduced functionalities on the SiNSs surface. This approach is currently under investigation and should open up new fields of applications.

The hybrid materials exhibit similar photoluminescence properties to the non-functionalized materials, namely an emis-

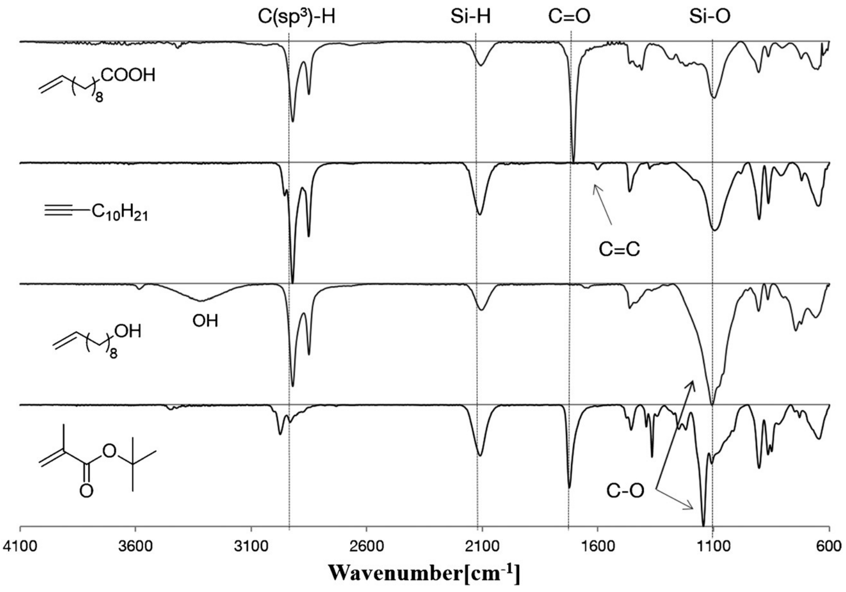


**Figure 5.** FTIR spectra of functionalized SiNSs by 4-DDB-induced hydrosilylation.

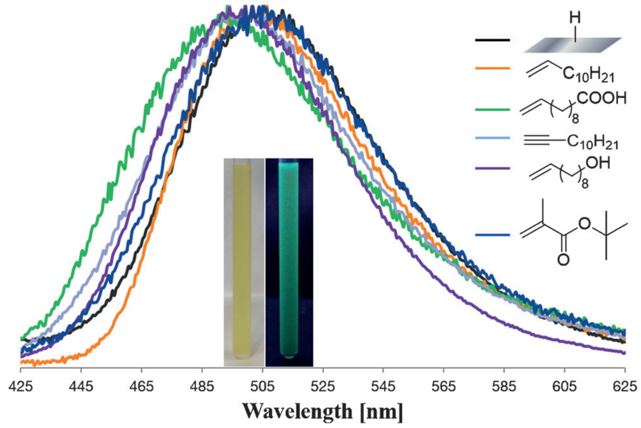


**Figure 6.** PL spectra of freshly etched and functionalized SiNSs by 4-DDB-induced hydrosilylation.

sion at $\lambda_{max} \approx 500$ nm (Figure 6, Figure S10 in the Supporting Information). This is in accord with the functionalized SiNCs which show similar PL for Si–H– and Si–C-capped SiNCs.[26]

In summary we present the first radical-induced hydrosilylation approach for the efficient functionalization of hydride terminated SiNSs. High temperatures (130 °C) or the addition of diazonium compounds successfully initiate the reaction. With this method SiNSs are functionalized with (non-)functional alkenes and alkynes, introducing alkyl, hydroxyl-, carboxy- and ester groups which improve the dispersibility properties. The free-standing SiNSs were found to have a thickness of about 2 nm and exhibit PL ($\approx 500$ nm). Additionally, we demonstrate that NMR experiments in solution can be used to show the successful functionalization of the SiNSs. The obtained functional hybrid materials should be valuable for subsequent reactions and open up possibilities for new applications, for example, in electronics or optoelectronic devices.

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**Keywords:** hydrosilylation · layered polysilane · nanotechnology · silicon nanosheets · surface chemistry

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