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Abstract. Alkanes such as n-hexane have been used as co-solvents in the production of functionalized semiconductor nanoparticles from alkenes and alkynes using Reactive High Energy Ball Milling (RHEBM) under the assumption that they are non-reactive under typical milling conditions. In this paper, we report on a comparative study with two hydrocarbon solvents of comparable chain length, 1-hexyne, and n-hexane, and their milling products using three different commercially available silicon precursors, namely single crystal silicon wafers and polycrystalline particles having a nominal size of 4 µm and 1 mm. We found that nanoparticle formation and surface functionalization in all the three silicon systems occurs only with 1-hexyne; n-hexane is non-reactive and does not lead to appreciable functionalized nanoparticle formation under the conditions studied. Nanoparticles (where formed) and microparticle byproducts of appropriate samples were characterized by TEM, FTIR, PL, $^{1}H/^{13}C$ NMR and TGA to separately confirm nanoparticle formation and surface functionalization.

Keywords: Silicon nanoparticles, saturated hydrocarbons, unsaturated hydrocarbons, 1-hexyne, n-hexane

Introduction

Reactive High Energy Ball Milling (RHEBM) is a specialized type of mechanochemical processing in which a solid surface can be functionalized by a reactive liquid in the milling process. Through the combination of particle size reduction (comminution) and surface functionalization, passivated nanoparticles can be formed which are soluble in the surrounding reactive liquid and easily separated from larger, less functionalized material. This procedure has been demonstrated using several solid-liquid combinations, but the most reported systems involve the reaction of silicon surfaces with short-chain alkenes and alkynes[1]. A co-solvent – presumed to be inert – is sometimes used along with the reactive ligand to provide sufficient liquid volume in the milling vial when it is prohibitive to use pure ligand (e.g., cost), to serve as a heat transfer medium to the vial walls for highly exothermic reactions, or to stabilized silicon nanoparticles against further oxidation[2]. Inert co-solvents have also been used in the formation of passivated silicon nanoparticles (SiNPs) using other techniques, such as in the thermal decomposition of diphenylsilane in mixtures of octanol and hexane under supercritical conditions[3]. In either case, it is desirable – though certainly not required – that the inert co-solvent be of comparable chain length to the reactive ligand to maximize nanoparticle solubility, for example, an equimolar mixture of 1-hexyne and n-hexane where the former is the reactive ligand and the latter the inert co-solvent. To date, there have been no studies confirming the non-reactivity of these alkane co-solvents in the RHEBM environment. The energy input to these systems can be large – on the order of 1 W/g,[4] and temperatures can increase during the milling operation if heat transfer is not properly controlled, so co-solvent inertness should not be assumed.

Herein we report on the comparison of reactivity and reaction products between two representative hydrocarbons, 1-hexyne and n-hexane, on SiNPs formed during RHEBM. Three different silicon sources are

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used to investigate differences in reactivity: ground silicon wafer and commercially available silicon particles with nominal sizes of 4µm and 1mm. Characterization techniques were selected that confirm nanoparticle formation and/or surface functionalization for the two target organic compounds.

Materials and Methods

The silicon starting materials were subjected to Reactive High Energy Ball Milling in organic liquids as previously described.[5] Characterization of surface bonding include X-Ray Photoelectron Spectroscopy (XPS), liquid phase Nuclear Magnetic Resonance (NMR) spectrometry, Fourier Transform Infrared (FTIR) spectroscopy, and Thermogravimetric Analysis (TGA).

Materials Three different silicon starting materials were utilized: Single crystal silicon wafer (Sigma-Aldrich, single side polished, undoped, mirror finished, 111 orientation, 3 in. diameter × 0.5 mm thick, undoped, 99.00% purity, 3-4 microohm-cm electrical resistivity @ 0 °C). Two commercial scale ground photovoltaic/ semiconductor-grade silicon wafer particulate materials with nominal sizes of 1mm and 4µm were also used (GlobeSil, Lexington, KY). Both commercial silicon particulates come from ingot processing and are undoped with at least 99.9999% purity.

Reagent grade 1-hexyne (Sigma-Aldrich, 99%, density 0.715 g/ml) and n-hexane (Sigma-Aldrich, 95%, density 0.678 g/ml) were purified by simple distillation upon receipt. NMR solvent dichloromethane-d_2, 99.5 atom% (CD_2Cl_2; 99.96%) was obtained from Sigma-Aldrich (99 atom % D). Hydrocarbons were distilled under nitrogen and stored over 3 Å molecular sieves and placed in a nitrogen-filled glove box.

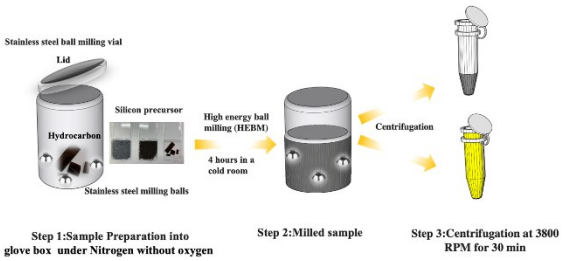


Fig. 1 Silicon particles hydrocarbons-passivated synthesis (SiPs@hydrocarbons) by RHEBM. Schematic diagram of the silicon particles with hydrocarbon synthesis. (SiPs@hydrocarbons) under nitrogen. Silicon precursor (5g) and hydrocarbon (22.0 g total) (1:4 %m/m) were added into a hardened stainless steel ball milling vial with three hardened stainless steel milling balls (1.2cm in diameter, 8.1g each) in a nitrogen filled glove box.

Surface Reactions in RHEBM. Silicon precursor (5g) and hydrocarbon (22.0 g total) were added to a hardened stainless steel milling vial along with three hardened stainless steel milling balls (1.2cm in diameter, 8.1g each) in a nitrogen filled glove box. The silicon wafer chunks varied in size and shape, with dimensions ranging from just under 1.0 cm to just over 1.5 cm. The commercial-grade silicon particulate sizes were as previously stated (4µm and 1mm). It is recommended that the loading of the vial does not exceed approximately 50% of the

available volume[6]; the reagent-grade organic liquid is added to the vial by weight so its volume varies from 20-25 mL depending on the solvent density.

The contents of the vial were subjected to RHEBM using a SPEX CertiPrep 8000D Mixer/Mill for 4 hours in a cold room. After RHEBM was complete the milled samples were separated into soluble (supernatant) and insoluble (pellet) fractions by centrifugation at 3800 RPM for 30 min (Fig 1). The supernatant was passed through a 200 nm in-line filter, the effluent from which was rotary-evaporated and pumped for 24 hours to remove any excess unreacted hydrocarbon, then weighed. The pellet material was also dried for 24 hours to remove any excess unreacted hydrocarbon, then weighed. The resulting supernatant solid product is labeled silicon nanoparticles (SiNPs) and the resulting pellet solid product is labelled silicon microparticles (SiMPs).

Process Yield for Nanoparticle Formation. Process yield was calculated from a ratio of the weight of SiNPs to the weight of silicon starting material (nominally 5g in each experiment). The contribution of hydrocarbon covalently bound to the surface of the nanoparticles was ignored because surface coverage (assumed to be relatively constant) is not known and because the yield values are only used for relative, comparative purposes.

XPS Spectra for Elemental Analysis. XPS measurements were conducted on a VG Scientific MKII system using a Mg Kα anode as excitation source ($h\nu$ = 1253.4 eV). The pressure in the chamber during analysis was $<5 \times 10^{-8}$ mbar. The samples were deposited on indium foil via evaporation and were 5 mm square and 4 mm thick. Spectral peak fitting and deconvolution was performed with CasaXPS using Gaussian-Lorentzian line shapes.

FTIR for Bonding Analysis. FTIR spectra were recorded at 1 cm^{-1} resolution with 2000 scans on a Thermo Nicolet Nexus 670 FTIR instrument, enabling easy measurement of the spectra of solids and liquids. For ATR, a few milligrams of SiNPs powder were placed on the optic window with a germanium glass and the compression clamp engaged to 6 psi to ensure good contact between the sample and the crystal.

PL Analysis. Photoluminescence spectra of supernatant solutions were taken with a Varian Cary Eclipse fluorescence spectrophotometer at room temperature in quartz cuvettes with an optical pathlength of 1.00 cm. All emission spectra were recorded with an excitation wavelength of 300 nm. PL data were acquired using a concentration of 3mg/mL for SiNPs@1-hexyne (in methanol). The silicon microparticles milled in n-hexane result in small amounts of particles not suitable for dispersion in methanol.

NMR for Structural Analysis ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, using a Bruker DSX 300 NMR. spectrometer, Deuterated dichloromethane (CD_2Cl_2) was used as a solvent. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm and are referenced to CD_2Cl_2 signals (δ=5.32 and 53.5 ppm, respectively).

TEM/SEM Images for Morphology. TEM-measurements were collected on a 300 kV FEI Tecnai G2 F30 Transmission Electron Microscope. SEM photomicrographs were acquired on a Hitachi 4800 High-resolution SEM, 1.0 nm resolution at 15kV. SiNPs samples were deposited on carbon films 48h prior to measurement in

each of the means of dispersion and dried in a vacuum. The size distribution of the nanoparticles was determined by ImageJ software[7] based on TEM images. Statistical analysis was obtained by measuring the diameters of 200 nanoparticles.

TGA Analysis. A TA Instruments TGA Q500 Thermogravimetric Analyzer/Pfeiffer was used in the temperature range of 25-1000°C with sample heating at the rate of 5° per minute under flowing nitrogen.

Results and Discussion

The milling of silicon in both dry and wet environments is well studied[8,9]. In fact, it has received renewed interest as silicon and silicon-based alloys and nanocomposites are strong candidates for anode materials in lithium-ion batteries[10]. A recent review of both wet and dry milling of silicon for this application highlights the advances and challenges[11]. Such milling parameters as milling time, ball/powder ratio, and milling media size have been studied for silicon in these non-reactive systems and showed that the d_{90} particle diameter of 12 µm did not change significantly from 4 to 8 hours of milling time in 20 mm grinding beads[12].

However, in the potentially reactive wet milling environments studied here, the evolution of nanoparticles follows a different path. Functionalized nanoparticles can be formed early in the milling process where they remain solubilized in the surrounding liquid and do not participate significantly in further size reduction. Traditional ball milling parameters like milling time, ball/powder ratio, and milling media size become less important in determining whether the liquid medium is reactive or not with the milled material.

As a result, nanoparticle formation is the key indicator of surface functionalization in these reactive milling systems[5], that is, only those particles that are sufficiently small and sufficiently surface functionalized will remain soluble in the reactant liquid mixture during centrifugation. As shown in Table 1, only silicon reacted with 1-hexyne resulted in surface-functionalized nanoparticles that could be recovered from the supernatant after centrifugation and filtration. The yields from all three silicon source materials functionalized with 1-hexyne are consistent with process yields in

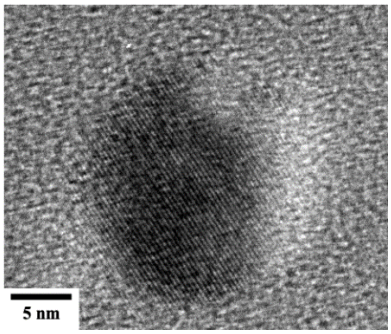
Table 1 Silicon Nanoparticles SiNP@1-hexyne Yield %

	Wafer	**GlobeSil 4µm**	**GlobeSil 1mm**
1-hexyne	9.4%	11.7%	7.6%

similar RHEBM systems.[1] Though yield could potentially be increased with the adjustment of milling parameters such as time, the four hour milling times here were sufficient to show that functionalized nanoparticles were formed only with 1-hexyne as a reactant liquid. Only impurity levels of solid material were recovered from the supernatant of centrifuged samples from the milling of silicon in n-hexane. This is

evidence that no significant reaction is occurring with n-hexane under these process conditions. As a result, characterization of SiNPs functionalized with 1-hexyne will first be discussed, followed by characterization of materials obtained from milling in n-hexane.

Silicon Milled in 1-Hexyne. The average sizes of nanoparticles formed from the reaction of silicon with 1-hexyne were 4.5 ± 1.6 nm, 3.1 ± 0.67 nm, and 2.1 ± 0.5 nm for the wafer, 4µm GlobeSil, and 1mm GlobeSil starting materials, respectively, as determined by TEM histograms (Figure 2, inset). Representative TEM images for the functionalized SiNPs from wafer and polycrystalline powders are shown in Figure 2. The nanoparticles derived from the wafer material show uniform lattice fringes with spacing of 0.080nm indicative of a single crystalline material. On the other hand, nanoparticles from the polycrystalline powder show lattice fringes which intersect along multiple boundaries with an interplanar spacing of 0.45 Å, indicating that the nanoparticles contain numerous single crystalline domains.



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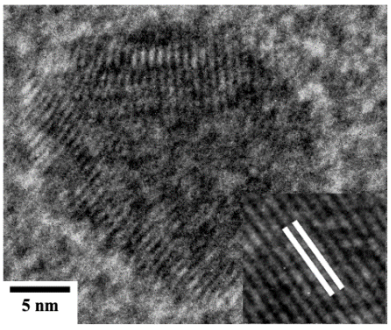

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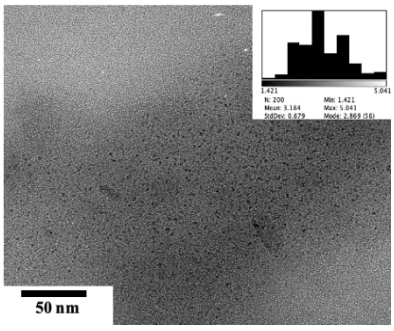


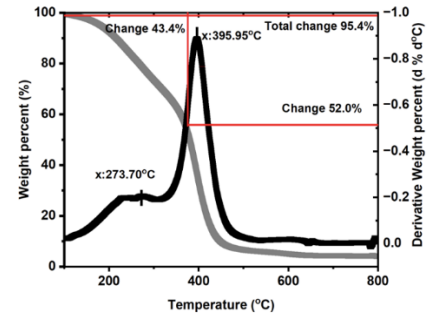
c

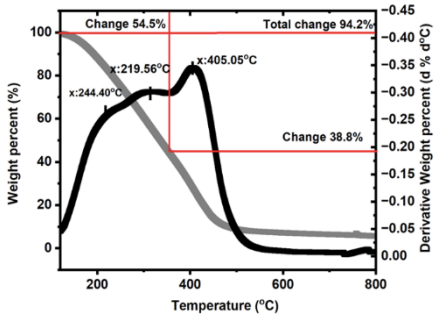
Fig.2.TEM images of major sphere shapes and various precursors, well dispersed and polycrystalline. TEM images of Si nanoparticles with scale bars: 5 nm (a from wafer, b from GlobeSil 1mm), 50 nm (c from GlobeSil 4mm)

All three 1-hexyne functionalized SiNPs are also characteristically photoluminescent (not shown) with a well-defined Stokes shift and emission in the 400-500 nm range as previously reported.[1] Since no SiNPs for the n-hexane reactions were obtained, neither TEM nor particle size analyses were performed.

Additional support reaction in the 1-hexyne system comes from TGA, FTIR, and NMR results.

Thermogravimetric analysis of the 1-hexyne functionalized silicon nanoparticles (Figure 3) shows similar overall weight losses in the range of 78-95%, but with different weight loss characteristics. In all samples, weight loss below about 200°C can be attributed to the loss of adsorbed water and residual organic solvent.[13,14] Wafer produced nanoparticles (top) show two distinct weight losses – the first broad weight loss above 200°C and the second more defined loss centered at 396°C as indicated by the derivative weight loss curve. GlobeSil 4µm-derived nanoparticles (Figure 3 middle) show a similar, but less defined mass loss with derivative peaks at 320°C and 406°C. GlobeSil 1mm-derived nanoparticles, however, show a steady polynomial-like decrease with no distinct mass loss events and a total loss of 78%.





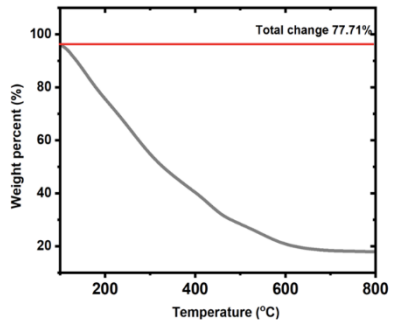


Fig. 3 Percentage (left axis) and derivative (right axis) weight loss curves with temperatures for SiNPs functionalized with 1-hexyne for wafer (top), 4µm GlobeSil (middle) and 1mm GlobeSil (bottom) starting materials.

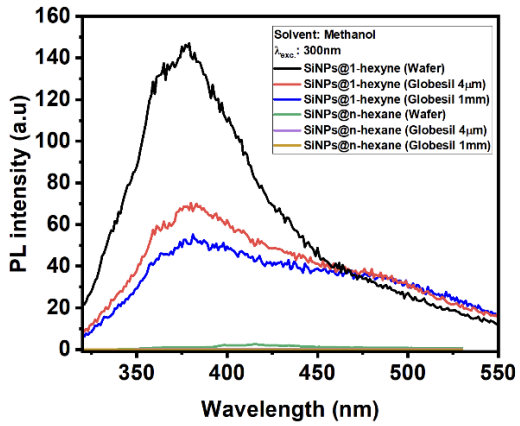


Fig. 4. Emission spectra in methanol of (black, red, and blue) SINPs@1-hexyne and (green, purple, and yellow) SiNPs@n-hexane. Emission spectra of SINPs@1-hexyne and SiNPs@n-hexane at = 300 nm, respectively.

Passivation of silicon nanoparticles with organic molecules is known to affect their photoluminescence (PL) properties[15]. In the case of 1-hexyne passivation, the resulting silicon nanoparticles exhibit a broad photoluminescence at approximately 374 nm when excited at 300 nm. The intense PL is likely due to the quantum size effects of the silicon nanoparticles or possibly due to surface trap states. On the other hand, when silicon is milled with n-hexane, the PL spectrum shows no significant emission when solutions are excited at 300 nm (Figure 4). This is due to the fact that the silicon microparticles are largely insoluble in methanol.

Figure 4 shows a comparison of the PL spectra of silicon nanoparticles solutions form milling in 1-hexyne and n-hexane, with the former showing a high intensity photoluminescence peak and the latter showing little or no emission.

The existence of a chemisorbed surface layer is further confirmed through FTIR analysis. Characteristic peaks for the terminal triple bond in 1-hexyne are at 2130 cm^{-1} and 2200 cm^{-1} and its associated acetylenic C-H stretching vibration is at 3337 cm^{-1}. A C-H bending vibration also appears at 950 cm^{-1}. The FTIR spectra of the 1-hexyne functionalized nanoparticles (Figure 5) however show none of this characteristic 1-hexyne vibrations but instead show vinylic C-H stretching bands at 2800-3000 cm^{-1}. Evidence of a weak olefinic stretch around ~1686 cm^{-1} is also observed. The pronounced peaks at ~1385 and ~1475 cm^{-1} correspond to CH bending vibrations of the alkyl chain and the ~947 cm^{-1} peak corresponds to a Si–C stretching vibration, indicating that the 1-hexyne is indeed bound covalently to the surface of the particle. Weak vibrational bands in the 950-1079 cm^{-1} region of the spectrum may be attributed to residual Si-O bonds on the surface.

Finally, NMR analysis of the functionalized nanoparticle solutions provides structural evidence of surface functionalization by 1-hexyne (Figure 6). In the ^{1}H NMR spectrum (Figure 6, top), resonances due to alkyl chain hydrogens (0.88 to 1.26 ppm) are evident as well as vinylic resonances spanning from 6.5 to 8.5 ppm. In the ^{13}C NMR spectrum (Figure 6, bottom) shows four resonances in the olefinic region at 125.9, 126.8, 129.4 and 138.4 ppm. Several resonances (15-50 ppm) appear in the alkyl carbon range of the spectrum. These results are consistent with previous studies of SiNPs functionalized with 1-octyne [4]. In this study, two primary bonding modes of the hydrocarbon with the silicon surface are proposed. The first is through a surface-bound silicon radical formed during milling which reacts via radical addition to alkyne forming a transient vinyl radical. This vinyl radical undergoes hydrogen abstraction with another 1-hexyne molecule in solution resulting in a surface bound alkene. The second structure is the result of [2+2] cycloaddition of the alkyne to silicon dimer surface pairs. [4,16]

Silicon Milled in n-hexane for the silicon precursors milled in n-hexane, direct comparison of potential reaction products with 1-hexyne is only possible for the microscale products since no nanoscale products were recovered in milling experiments with n-hexane after centrifugation. For these microscale products, NMR analysis was not possible because they were not soluble in any NMR solvent, and TGA analysis was not helpful as less than 1% weight loss was observed in all microscale samples due to the lower surface-to-volume ratio of these larger particles. As a result, the key comparative technique for microscale materials was XPS.

XPS provides the most compelling evidence for a lack of C-H activation in n-hexane milled silicon. As shown in Figure 7, a comparison of XPS results for silicon milled in 1-hexyne (middle spectra for all three silicon sources) with silicon milled in n-hexane (bottom spectra for all three silicon sources) shows the presence of a Si-C environment centered at 100-101eV [17-19] (green peak) in microscale silicon milled in 1-hexyne that does not exist for microscale products milled in n-hexane. In fact, the n-hexane milled microscale products do not differ substantially from the unmilled silicon precursors (Figure 7, top spectra) where both metallic silicon peaks at 98-99 eV and a broad Si-O_x silicon suboxide peak at 102 eV are evident. [20,21]

Conclusions

Silicon nanoparticles (SiNPs) surface functionalized with 1-hexyne in Reactive High Energy Ball Milling (RHEBM) were formed from three different silicon sources. Silicon wafer and commercially available silicon of two different particle sizes (4 µm and 1mm) produced functionalized nanoparticles of nominal size 3 nm when milled in 1-hexyne and were subsequently characterized by spectroscopy and weight loss techniques to provide evidence of functionalization. These same three silicon sources milled with n-hexane, however, did not lead to appreciable nanoscale material indicating lack of surface functionalization in this system. Furthermore, surface characterization of the n-hexane milled silicon microscale products produced insufficient evidence of Si-C bonds as determined by FTIR and XPS to support surface functionalization independent of nanoparticle formation. We thus conclude that n-hexane can be considered an inert co-solvent in RHEBM processes under these conditions.

These findings are limited to the inertness of n-hexane only but have implications to the use of other straight-chain hydrocarbons in RHEBM, especially n-alkanes. Just as we have shown that the formation of functionalized silicon nanoparticles in 1-octyne was extensible to a variety of other alkynes, alkenes, and alkanes with other terminal functional groups[1], the inertness of n-hexane as a co-solvent suggests that other short-chain n-alkanes may be similarly suitable as inert co-solvents. The use of inert co-solvents in RHEBM is important from a cost reduction standpoint as n-alkanes are less expensive than their alkene or alkyne counterparts and the amount of reactive liquid for surface reactions is generally small. In future work the previously assumed non-reactivity of other common co-solvents such as benzene and toluene should be studied.

Associated Content

Supporting Information

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials. Moreover, the raw data are available from the corresponding author (JPV) upon reasonable request. These data include physical appearance of the starting materials, synthetic procedure of SiNPs, samples characterization, XPS, and NMR data.

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Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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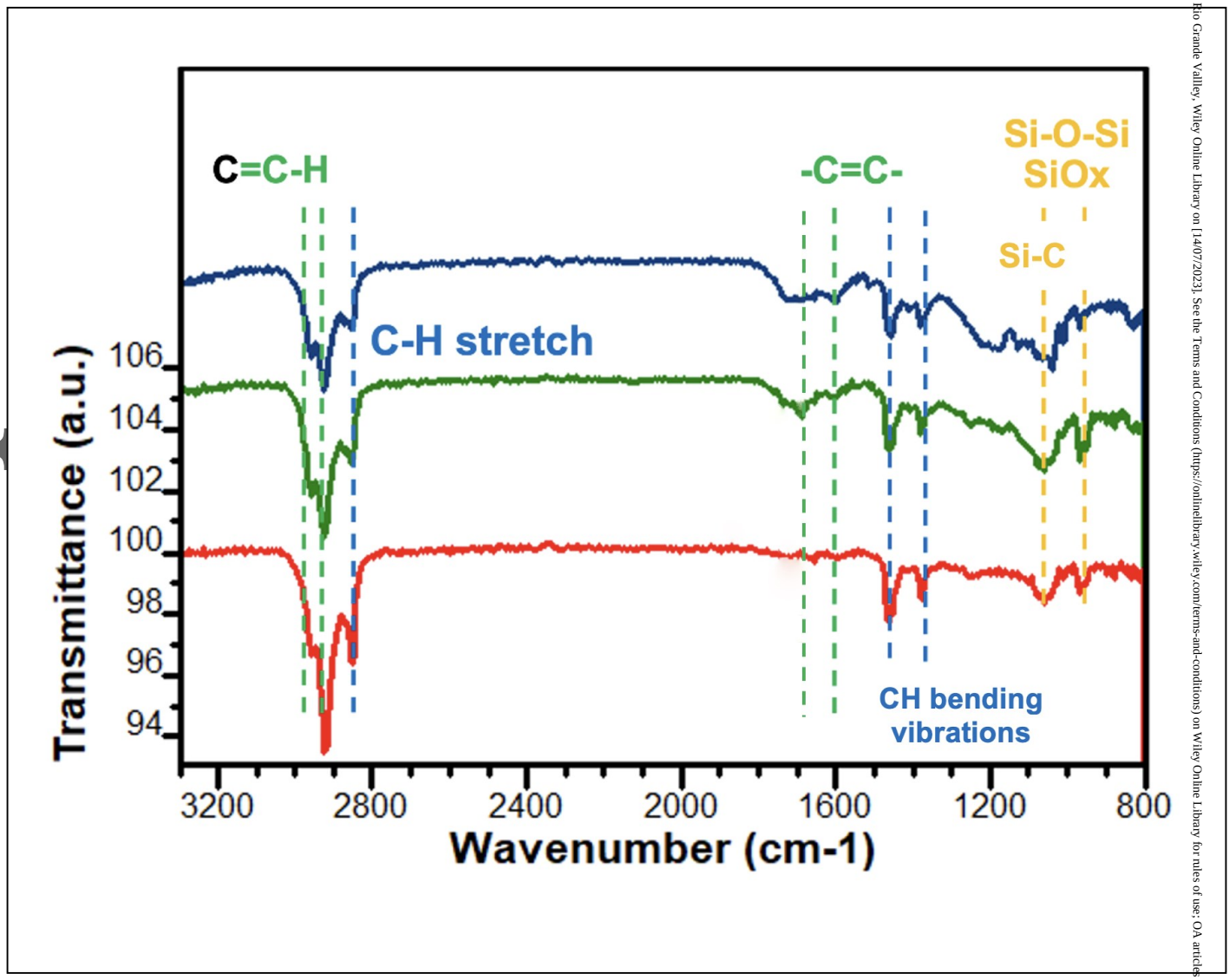


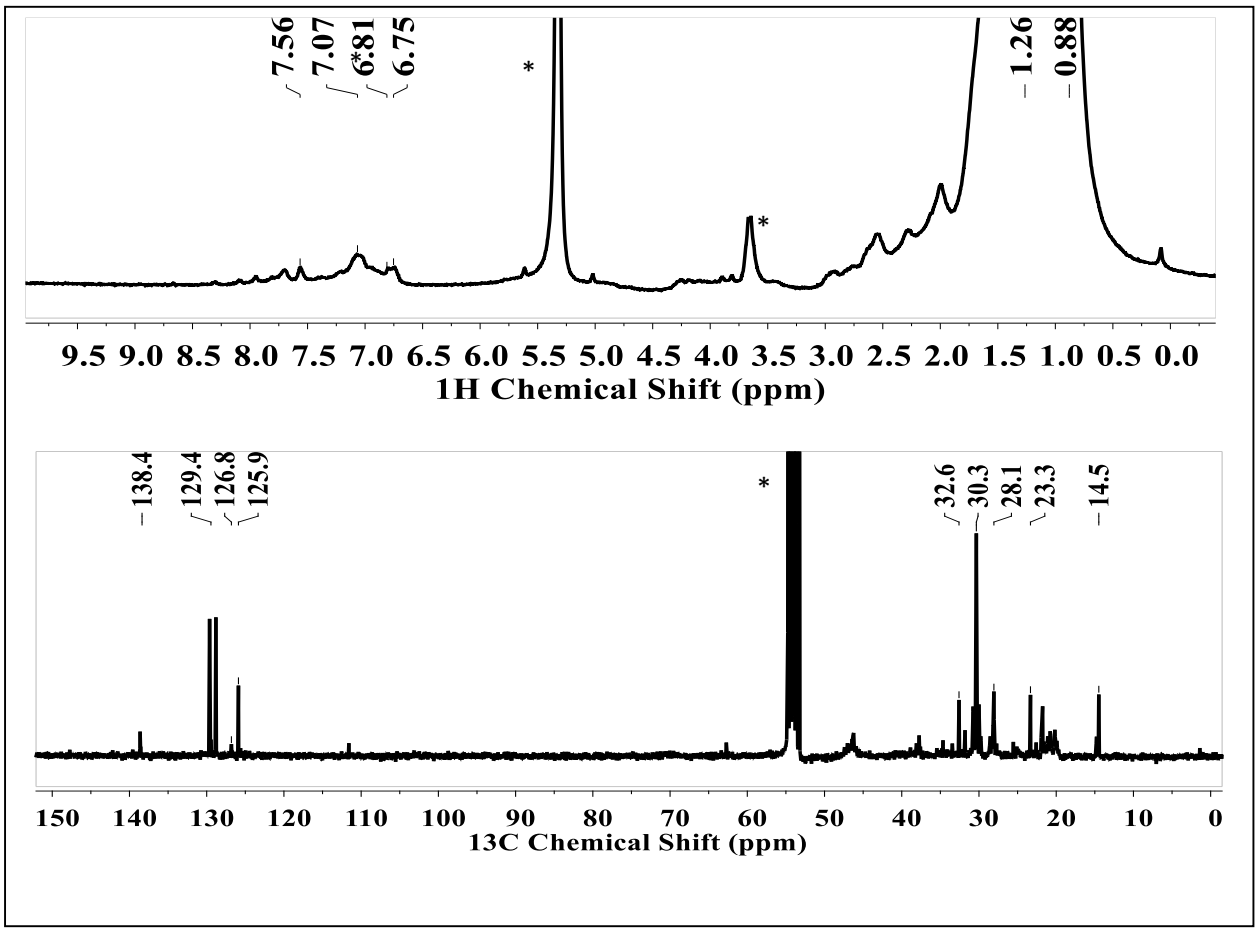
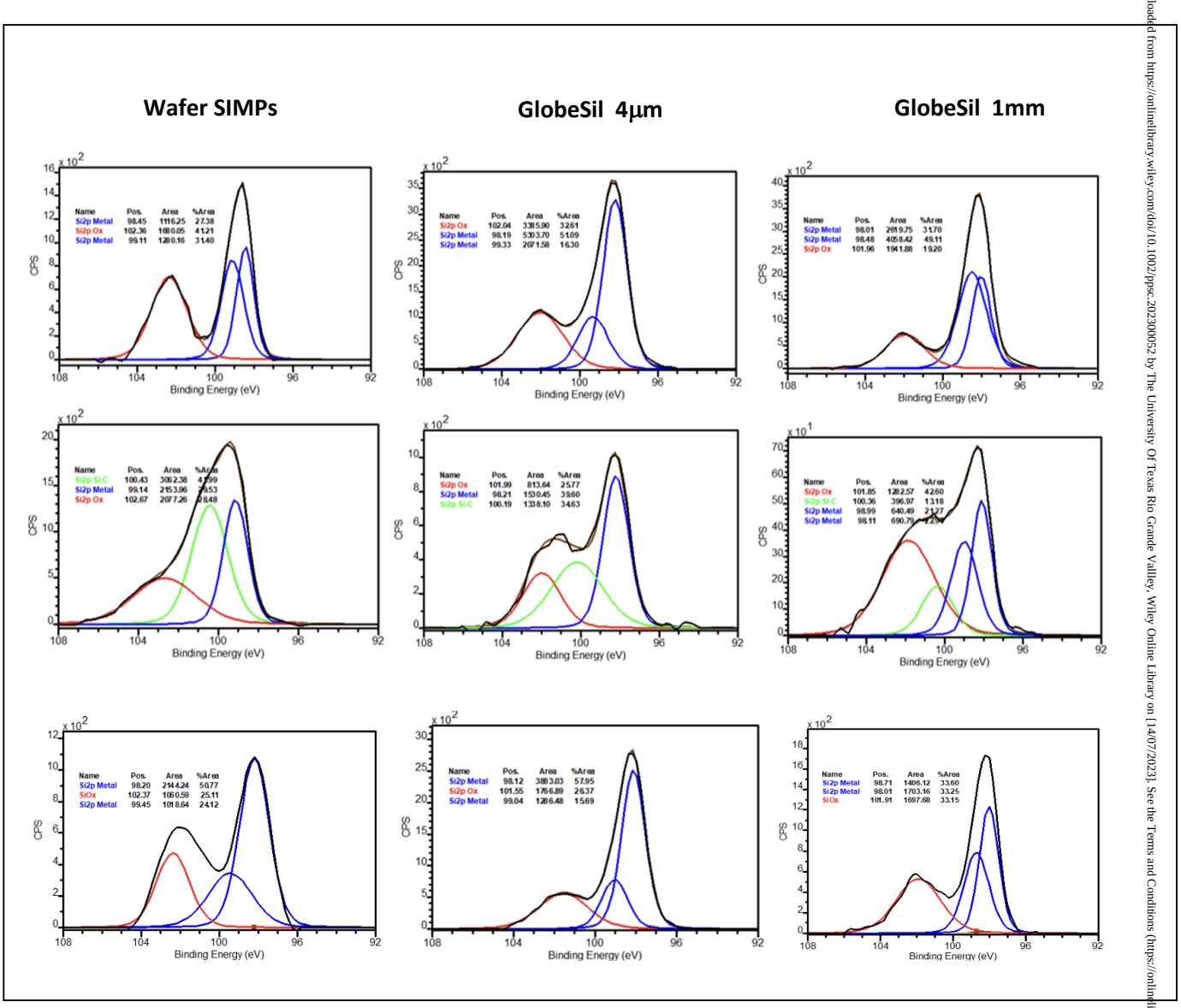


Fig. 6 ^{1}H NMR (top) and ^{13}C NMR spectra of 1-hexyne functionalized SiNPs from wafer. * Residual dichloromethane d-2 and ** milling impurities.



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