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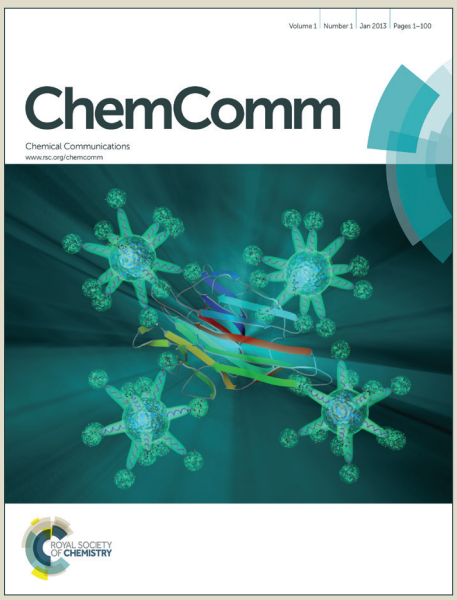

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Rapid, Metal-free Hydrosilanisation Chemistry for Porous Silicon Surface Modification

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M. J. Sweetman, S. J. P. McInnes, R. B. Vasani, T. Guinan, A. Blencowe and N. H. Voelcker*[a]

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Here, we report on a novel surface modification for porous silicon (pSi). Hydroxyl-terminated pSi surfaces are modified with a hydrosilane via Si-H activation using the Lewis acid catalyst tris(pentafluorophenyl) borane. This surface reaction is fast and efficient at room temperature, and leads to a surface stabilised against hydrolytic attack in aqueous media. The resulting surface shows promise as a substrate for surface-assisted laser desorption/ionisation mass spectrometry.

Porous silicon (pSi) has been widely used as a novel material in the biomedical, sensing and optoelectrical fields, with applications including cell culture substrates,[1] drug delivery vehicles,[2] biosensors[3, 4] and photoelectrochemical devices.[5, 6] Favourably suited to a diverse range of applications due to its biocompatibility, high internal surface area (200 – 800 m^2/g) and inherent optical properties, research into pSi-based devices and materials continues to progress at a rapid rate.[7] For each application, it is highly important to generate pSi surfaces with the appropriate chemical functionality and level of stability/degradability. To date, there are a number of surface functionalisation techniques that utilise the highly reactive nature of the freshly prepared hydride-terminated pSi surface.[8]

Hydrosilylation with ω-functional alkene or alkyne species has become one of most common functionalisation techniques of the freshly etched Si-H terminated pSi surface.[9] This reaction has to be performed under strictly inert conditions to avoid oxidation side reactions, and even then the reaction yield is often insufficient: residual Si-H groups are susceptible to hydrolytic attack in aqueous media resulting in corrosion of the pSi surface.[10] Deliberate surface oxidation to generate Si-OH groups followed by silanisation with alkoxy or chloro-silane species is another popular technique that can introduce specific chemical functionality and stabilise the pSi surface.[11, 12] But the drawback is that silane surface coverage can be patchy, and polysiloxane networks can easily form.[13]

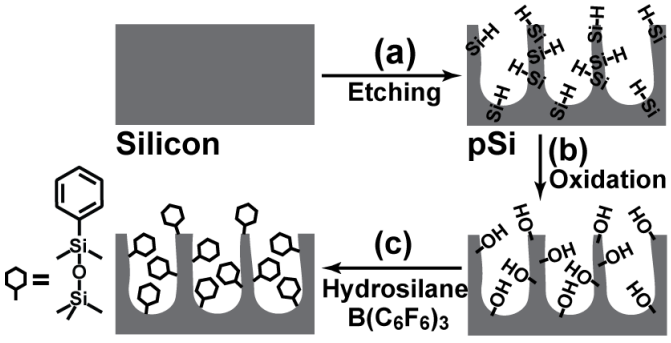
Recently, surface modification of pSi via thermal hydrocarbonisation or thermal carbonisation have gained interest due to the excellent stability of the resulting surfaces in aqueous media.[14-16] While these surface modifications generate a highly stable pSi structure, they are often challenging to further chemically functionalise.[17]

One application that highlights the requirement for precise pSi surface functionality is surface-assisted laser desorption/ionisation mass spectroscopy (SALDI-MS).[18] This technique is highly dependent on achieving a specific chemical functionality on pSi, in order to obtain high quality mass spectra and a low limit of detection for an analyte of interest.[19] Commonly, hydrophobic surface chemistry is desired for SALDI-MS applications.

Therefore, it is of great interest to develop new pSi surface modification techniques in order to find compatible, efficient and high grafting density procedures to generate stable and functional surfaces. In this report, we describe a novel chemical functionalisation procedure for pSi, whereby a hydrosilane is grafted to hydroxyl-terminated (oxidised) pSi surfaces via Si-H activation with the catalyst tris(pentafluorophenyl) borane. This procedure is based upon hydrosilane grafting to silica surfaces, where fast reaction times and excellent hydrosilane coverage have been recently reported.[20] This new pSi functionalisation method will considerably extend the application of pSi based materials. Hydrosilane compounds used in this reaction are moisture and air stable, providing a distinct advantage over pSi functionalisation with alkoxy and chloro silane compounds. This surface modification procedure provides further advantages over the abovementioned existing pSi modification routes. The reaction time (~ 5 min) is far superior to hydrosilylation reactions (reaction times of 3 – 24 h) and the reaction mechanism avoids the formation of polysiloxane networks on the pSi surface, which are a problem for silanisation reactions. The simplicity and efficiency of the reaction and stability of the reagents make this a highly attractive method for pSi surface modification.

We describe here the first example of this type of activated hydrosilane grafting to oxidised pSi surfaces. The resulting grafted surfaces were fully characterised via infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). ToF-SIMS has been used to cross-sectionally profile the chemical composition of the pSi films, a characterisation method often overlooked for pSi. ToF-SIMS was also employed to characterise functionalised pSi microparticles (pSi MPs). Water contact angle measurements were recorded to illustrate the effect of grafting a hydrophobic silane onto pSi. Finally, one specific application is demonstrated, where a hydrosilane functionalised pSi surface is successfully used for SALDI-MS based detection of an illicit substance.

Three specific pSi surfaces were prepared that allowed efficient characterisation of the hydrosilane grafting procedure by the analytical techniques mentioned above. Generally, pSi was prepared by electrochemically etching a silicon wafer in an aqueous hydrofluoric acid (HF)/ethanol solution. Variation of the etching conditions (HF:ethanol ratio, etching current and time, and resistivity of silicon) allowed the fabrication of the three discrete pSi surface types. Specific etching parameters are described in the ESI†. High resistivity silicon (3 – 6 Ωcm) was used to prepare pSi for IR measurements, while low resistivity silicon, of < 0.002 Ωcm was used to prepare pSi for ToF-SIMS and 0.008 – 0.0012 Ωcm resistivity silicon was used to prepare pSi for the other characterisation techniques. The reported hydrosilane grafting procedure relies on an oxidised (Si-OH terminated) pSi surface to work. Therefore, pSi surfaces were either ozone oxidised (15 min exposure to 3.2 g/h ozone), or thermally oxidised (1 h at 500 °C) in order to generate terminal hydroxyl groups. Following oxidation, the hydrosilane grafting procedure was performed, which involved adding the oxidised pSi surface to a solution of dimethylphenylsilane (DMPS) and tris(pentafluorophenyl) borane catalyst dissolved in dichloromethane (DCM). The reaction was performed in a closed vessel and was agitated at room temperature for 2 – 10 min to allow for completion of the reaction on the highly porous surface. Small bubbles of hydrogen gas were observed evolving from the pSi film during the procedure, as the reaction is dehydrogenative.[20] Hydrogen evolution ceased once the reaction had reached completion. The pSi surface was removed and washed with copious amounts of DCM and dried under a stream of N_2 gas. The overall surface fabrication and functionalisation procedure is shown in Scheme 1.



Scheme 1 Fabrication and modification of functionalised pSi surfaces. (a) Electrochemical etching of bulk silicon in HF solution, (b) oxidation of freshly etched pSi surface by ozone or thermal treatment and (c) grafting of DMPS using the catalyst tris(pentafluorophenyl) borane.

As shown in Fig. 1, the water contact angle of the ozone oxidised pSi surface is approximately 9°, which is expected, due to the hydrophilic hydroxyl groups across the surface. The contact angle increases dramatically to 131° for the DMPS functionalised pSi surface due to the hydrophobic nature of the silane. The large increase in contact angle also indirectly indicates a high surface coverage of the silane.

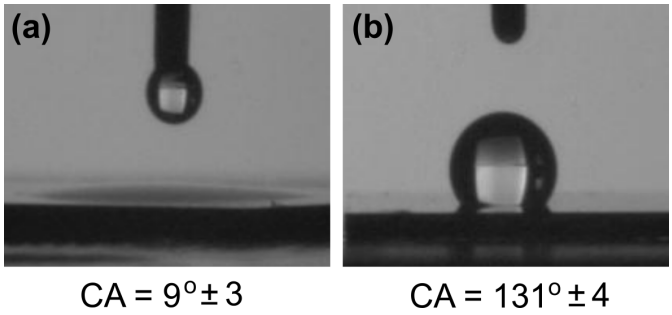


Fig. 1 Representative static water contact angles of (a) ozone oxidised pSi surface and (b) DMPS functionalised pSi surface.

The functionalised pSi surfaces were studied by IR spectroscopy (Fig. 2), where a clear symmetric deformation mode for $-CH_3$ was observed at 1252 cm^{-1}, along with peaks for C-H bending at 1460 cm^{-1}.[21] Asymmetric vibrational modes of $-CH_3$ around 2940 cm^{-1} and aromatic vibrational modes around 3050 cm^{-1} for the DMPS functionalised pSi were also seen (Fig. 2(b)).[22, 23] The broad Si-O stretching band at 1060 cm^{-1} corresponds to both the oxidised and hydrosilane modified surfaces as expected. However, the intensity of the SiO-H peak at 3390 cm^{-1} that dominates the IR spectrum of the oxidised surface, along with the shoulder at 960 cm^{-1}, corresponding to Si-OH (Fig. 2(a)), both disappeared following the hydrosilane modification.[24, 25] These results confirm that the Si-OH functional groups have reacted with the silane to generate Si-O-Si functionalities.

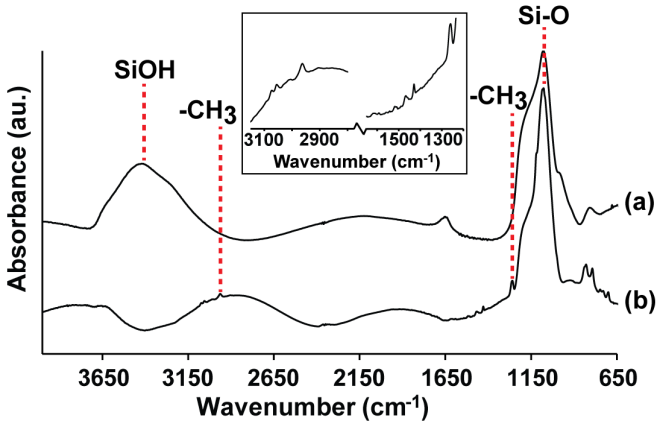


Fig. 2 IR spectra of (a) ozone oxidised pSi surface and (b) DMPS functionalised pSi surface. Insert shows a zoom of the relevant spectral regions for the DMPS pSi surface.

XPS was also used to characterise the chemical functionality of the oxidised and hydrosilane modified pSi surfaces. Table 1 shows the atomic percentages of the various elements present on an ozone oxidised and DMPS functionalised pSi surface, respectively. A conspicuous increase in the carbon content and C/Si ratio was observed following the hydrosilane grafting, with corresponding decreases in the O1s and the Si2p content, consistent with the presence of a carbon-rich surface layer. The attenuation of the O/Si ratio following hydrosilane functionalisation is indicative of the additional Si on the surface from the DMPS. The presence of

fluorine is due to residual amounts of fluorine attached to the surface after the electrochemical etching process in HF ethanol mixtures.[26] Deconvolution of the high resolution C1s spectrum of the DMPS functionalised pSi surface (ESI, Fig. S1) revealed a peak at 285.0 eV and a small π-π* satellite peak at 291.8 eV, corresponding to the phenyl group in the DMPS.[21, 27]

Table 1 Atomic percentages for the elements present in both an ozone oxidised and DMPS functionalised pSi surface.

Sample	C1s %	O1s %	Si2p %	F1s %	C/Si	O/Si
Ozone Ox.	2.9	47.0	48.8	0.42	0.05	0.96
DMPS	19.5	36.6	42.9	0.44	0.45	0.85

To verify that the hydrosilane grafting had occurred evenly throughout the pSi layer, cross-sections of thermally oxidised pSi films before and after functionalisation were imaged by ToF-SIMS, to detect characteristic positive ion fragments. Fig. 3 shows ToF-SIMS images of the total positive ions and the intensity of the selected positively charged fragments CH_3Si^+ (*m/z* approx. 43 amu), $C_6H_5Si^+$ (*m/z* approx. 105 amu) and $C_8H_{11}Si^+$ (*m/z* approx. 135 amu) characteristic of DMPS. As expected, little to no signal was detected for the CH_3Si^+, $C_6H_5Si^+$ and $C_8H_{11}Si^+$ positive fragments within the oxidised porous layer of the control sample. In contrast, all positive ion fragments were observed after hydrosilane functionalisation. The ToF-SIMS image also shows that the hydrosilane was present in an even distribution throughout the porous layer without any loss of signal intensity with increasing layer depth. It should be noted that in order to facilitate the ToF-SIMS imaging, a very thick pSi film (61.8 µm) was used (a corresponding cross-sectional SEM image of this pSi film is displayed in the ESI, Fig. S2(b)).

A second common form of pSi, namely pSi MPs was also functionalised via the hydrosilane grafting procedure. pSi MPs are of interest for drug delivery applications.[28] ToF-SIMS imaging of pSi MPs after functionalisation showed the same characteristic mass fragments CH_3Si^+, $C_6H_5Si^+$ and $C_8H_{11}Si^+$ (ESI, Fig. S3). As expected, mapping these fragments on the oxidised pSi MPs showed only a very weak intensity.

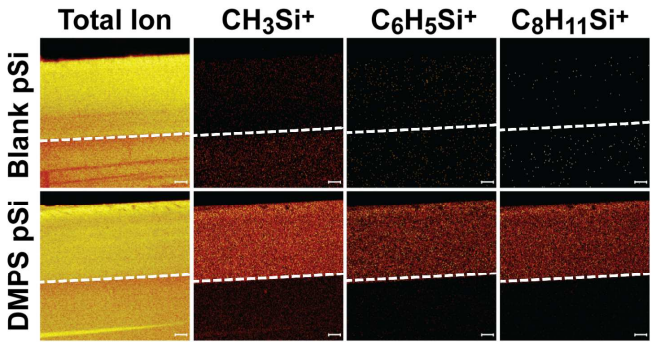


Fig. 3 ToF-SIMS images (100 µm x 100 µm) for the total positive ions and for the positively charged fragments CH_3Si^+ (*m/z* approx. 43 amu), $C_6H_5Si^+$ (*m/z* approx. 105 amu) and $C_8H_{11}Si^+$ (*m/z* approx. 135 amu) characteristic of the DMPS acquired on the cross-section of oxidised pSi and DMPS functionalised pSi films. The dashed line represents the interface of pSi (above line) and bulk silicon (below line). Scale bar on the images = 10 µm.

This surface analytical data lay the foundation for exploring and utilising this new surface modification procedure on pSi. As previously alluded to, selecting the appropriate surface chemistry, coverage and stability on pSi is of paramount importance when designing and fabricating specialised sensors and devices. As pSi based devices move from the laboratory into practical settings, this surface grafting procedure makes an important addition to the toolbox of chemical functionalisation methods.

Indeed we observed that the hydrosilanisation produces a surface that gives excellent performance in SALDI-MS of small molecules. Figure 4 (a) shows a representative SALDI mass spectrum for methadone on DMPS functionalised pSi at a physiologically relevant concentration of 1 µg/mL. A characteristic fragment peak for methadone is observed at m/z 265, with intensity comparable to results previously achieved for fluorosilane functionalised pSi surfaces. However, the required laser energy was 1 %, lower than for fluorosilane functionalised pSi which allows softer ionisation with less fragmentation a much lower laser intensity.[19] In contrast an ozone oxidised surface (figure 4 (b)) at the same methadone concentration, did not show any m/z peaks corresponding to methadone. The peaks observed in this spectrum are characteristic of pSi and arise due to a much higher laser energy (56 %).

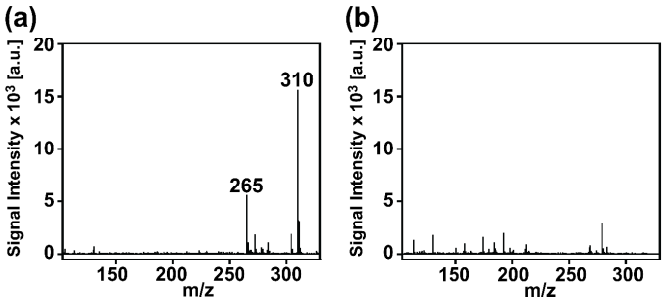


Fig. 4 Representative SALDI-MS spectra for methadone (m/z approx. 310) at 1 µg/mL on (a) DMPS functionalised pSi and (b) ozone oxidised pSi surfaces. A characteristic fragment peak for methadone is observed at m/z 265 from the DMPS pSi surface, but not for the ozone oxidised pSi surface.

In this report, we focussed on using only one hydrosilane to efficiently demonstrate and analyse the grafting procedure. However, this catalysed grafting reaction is compatible with hydrosilanes containing a wide range of terminal chemical functionalities, including amine, carboxylic acid, azide, thiol, alcohol and ester,[20] which should allow for fast and efficient, one-step surface modification on pSi. Currently, in order to introduce these surface chemistries on pSi, hydrosilylation or silanisation reactions are required which require stringently inert conditions or can produce undesired multilayers, respectively. In comparison, the hydrosilane grafting procedure presented here should allow the majority of desirable chemistries to be introduced onto pSi through one simple and fast reaction. This will be the focus of future work using this procedure on pSi surfaces. Future use of this reaction chemistry

will be vital for specialised applications in drug delivery, biosensor platforms and SALDI-MS.

Notes and references

[a] *ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, Mawson Institute, University of South Australia.*
Email: nico.voelcker@unisa.edu.au

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† Electronic Supplementary Information (ESI) including experimental techniques, pSi fabrication, C1s XPS spectrum, SEM characterisation and ToF-SIMS of pSi MPs is available: See DOI: 10.1039/c000000x/

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