Electronic Supplementary Material (ESI) for ChemComm.


**Supporting Information**

# Differential functionalisation of the internal and external surfaces of carbon-stabilised nanoporous silicon

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# 1 Materials and methods

## 1.1 Reagents, materials and solutions

P-type, boron doped, 0.55-1.00 mΩ cm resistivity, (1 0 0)-oriented crystalline silicon wafers were purchased from Siltronix, France. Hydrofluoric acid (HF, 48%w/w) was purchased from Scharlau (Australia), 10-undecanoic acid was purchased from Alfa Aesar (Australia). N-hydroxysuccinimide (NHS), N-(3-dimethylaminopropyl)N'-ethylcarbodiimidehydrochloride (EDC), ethanolamine, phosphate buffered saline (PBS) and 2-(N-morpholino)-ethanesulfonic acid (MES) tablets, poly(ethylene glycol) bis(amine) ($M_w$ = 3000, PEG-bis(amine)), fluorescein isothiocyanate (FITC), pentafluorophenol (PFP), and N,N-diisopropylethylamine (DIEA) were purchased from Sigma-Aldrich (Australia). Sodium hydroxide (NaOH, AR grade) was purchased from Merck (Australia). Cyanine5 amine (Cy5-amine) was purchased from Lumiprobe (USA).

## 1.2 Fabrication of pSi films

pSi films were produced from p-type silicon by electrochemical etching in HF-based solution. First, the parasitic layer was removed (Chamard et al., 1998; Sciacca et al., 2011) by applying a current density of 68 mA $cm^{-2}$ for 30 s in a solution of 3:1 of HF to ethanol. Then, this parasitic layer was dissolved in 0.1 M NaOH aqueous solution and thoroughly rinsed with MilliQ water and ethanol, then dried under a $N_2$ flow. The pSi film was generated by electrochemical etching under galvanostatic conditions in a 3:1 solution of HF to ethanol, applying a constant current density of 54 mA $cm^{-2}$ for 22 min. Next, the HF-based electrolyte was removed, and the sample was thoroughly washed with MilliQ water and ethanol, then dried under a $N_2$ flow. Immediately after etching, the prepared pSi film was functionalised.

## 1.3 Chemical modification of pSi films

Freshly etched pSi samples were thermally hydrocarbonised following a previously reported procedure (Jalkanen et al., 2014). Briefly, the freshly etched pSi samples were placed in a quartz tube and purged with $N_2$ for 45 min at a flow rate of 2 L $min^{-1}$. Then, acetylene gas was introduced together with $N_2$ into the tube at a ratio of 1:1 acetylene/$N_2$ for 15 min. After this time, the quartz tube was introduced into a tubular furnace preheated at 525 °C. After 14 min 30 s, the acetylene flow was interrupted, and after 15 min the quartz tube was removed from the furnace. The tube was then allowed to cool down to room temperature under a $N_2$ flow before the pSi samples were removed. Then, carboxylic acid functionality was introduced by thermal hydrosilylation with 10-undecanoic acid at 150 °C for 12 h in a $N_2$ environment. Then, the functionalised samples were thoroughly rinsed with ethanol and dried under a $N_2$ stream.

### 1.3.1 External functionalisation of pSi films

After functionalisation with 10-undecanoic acid, the ester activation of the carboxylic acid groups on the external pSi surface was performed in aqueous phase by incubation for 20 min with 20 mM EDC and 65 mM NHS in 0.1 MES buffer, pH 5.5, at room temperature. Subsequently, the sample was incubated in 100 μg $mL^{-1}$ PEG-bis(amine) in PBS for 1 h, then thoroughly washed with PBS and dried under a $N_2$ stream. To fluorescently label the amine functionality, the sample was incubated in a 10 μg $mL^{-1}$ FITC solution in PBS for 15 min, protected from light, and subsequently thoroughly washed with PBS and dried with a $N_2$ stream.

### 1.3.2 Internal functionalisation of pSi films

The externally modified pSi sample was incubated into a 0.2 M EDC, 0.2 M PFP and 0.2 M DIEA mixture in absolute ethanol (30 min, at room temperature). Afterwards, the pSi sample was rinsed with absolute ethanol, and dried under a $N_2$ stream. Fluorescent labelling was performed by incubating the sample with 10 μg $mL^{-1}$ Cy5-amine solution in PBS for 30 min. Finally, the sample was washed with PBS, dried under $N_2$ and stored in the dark.

## 1.4 Characterisation of pSi films after surface modification

### 1.4.1 Scanning Electron Microscopy (SEM)

For SEM imaging of the pSi surfaces, samples were mounted on an aluminium stub with double-sided carbon tape. Samples were imaged with a FEI Nova field emission gun scanning electron microscope using an InLens detector in high-resolution mode and an accelerating voltage of 10 kV.

### 1.4.2 Infrared (IR) spectroscopy

The surface functionalisation was characterised after each chemical modification step using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). A Thermo Scientific Nicolet 6700 FTIR instrument coupled to a diamond detector was used to collect spectra with a resolution of 4 $cm^{-1}$, after averaging 64 scans. Background spectra were blanked using air. The data were processed using OMINC software.

### 1.4.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analysis was performed using either an AXIS Ultra DLD or an AXIS Nova spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al Kα source at a power of 180 W (15 kV × 12 mA), a hemispherical analyser operating in the fixed analyser transmission mode, and the standard aperture (analysis area: 0.3 mm × 0.7 mm). The total pressure in the main vacuum chamber during analysis was typically between $10^{-9}$ and $10^{-8}$ mbar.

### 1.4.4 Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

ToF-SIMS measurements were performed using a Physical Electronics Inc. PHI TRIFT V nano ToF instrument (Chanhassen, MN, USA) equipped with a pulsed liquid metal $Au^+$ primary ion gun (LMIG), operating at 30 kV. The extractor current of the ion source was maintained at 3 μA. Surface analyses were performed using "bunched" $Au_1$ beam settings for surface imaging and spectroscopy. Mass calibration of the spectra was done with $CH_3^+$, $C_2H_5^+$, and $C_3H_7^+$ ions. Experiments were performed at high vacuum (< $10^{-8}$ mbar) and in the static mode (i.e. below $10^{12}$ ions $cm^{-2}$) to minimise sample damage.

### 1.4.5 Water contact angle measurements

Water contact angle measurements were conducted using a custom-built goniometer, with a Panasonic CCTV camera (WV-BP550/G) to capture the drop-surface images. A 3 μl drop of MilliQ water was deposited onto each surface using a 10 μL syringe. A photograph was immediately captured and contact angles were determined using ImageJ (v1.50i, NIH, USA).

### 2.5.6 Confocal microscopy

Confocal fluorescence microscopy images were obtained using an inverted Carl Zeiss LSM710 confocal microscope with an EC Plan-Neofluar 20x/0.30 M27 objective. The pSi surfaces were excited at wavelengths of 485 and 640 nm and emission was collected in a 576 – 701 nm range.

## 2 Supplementary Figures

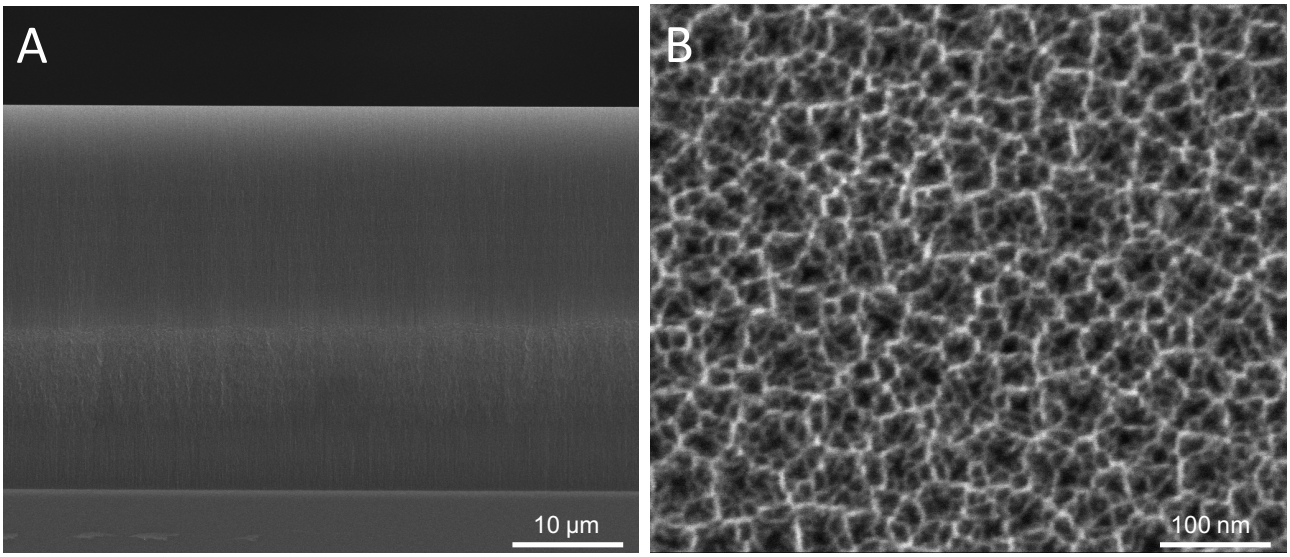


**Fig. S1.** SEM micrographs of freshly-etched pSi in (A) cross-sectional and (B) top views.

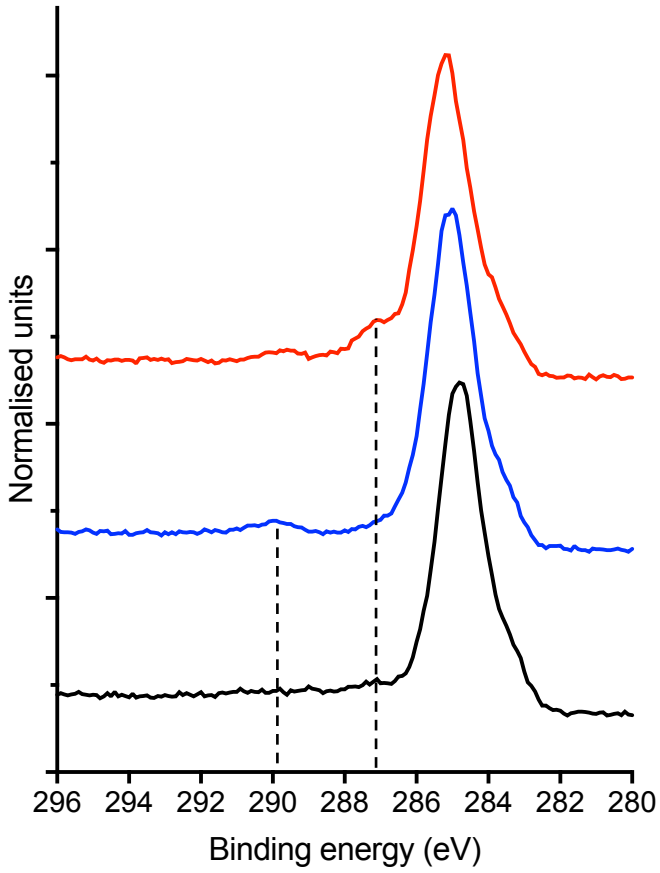


**Fig. S2**. XPS high resolution C 1s spectra for THCpSi (black); thermally hydrosilylated THCpSi (blue), and externally functionalised THCpSi with PEG-(bis)amine (red). The position of spectral features discussed in the main text are marked with dashed lines.

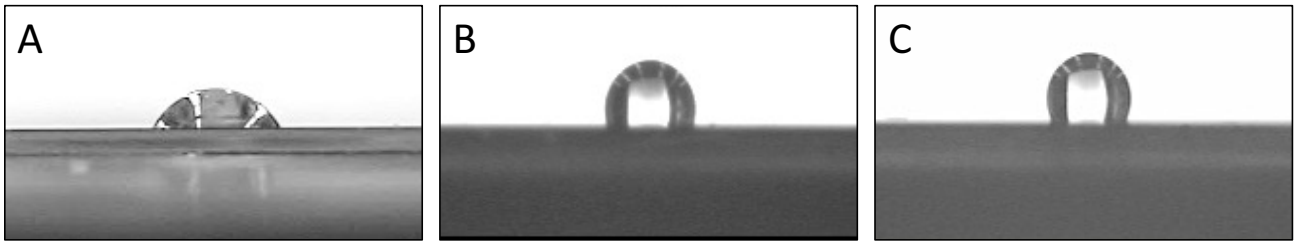


**Fig. S3.** Representative static deionised water (pH 5.5) contact angles of (A) freshly-etched pSi; (B) THC-treated pSi; and (C) THCpSi after thermal hydrosilylation with 10-undecanoic acid.

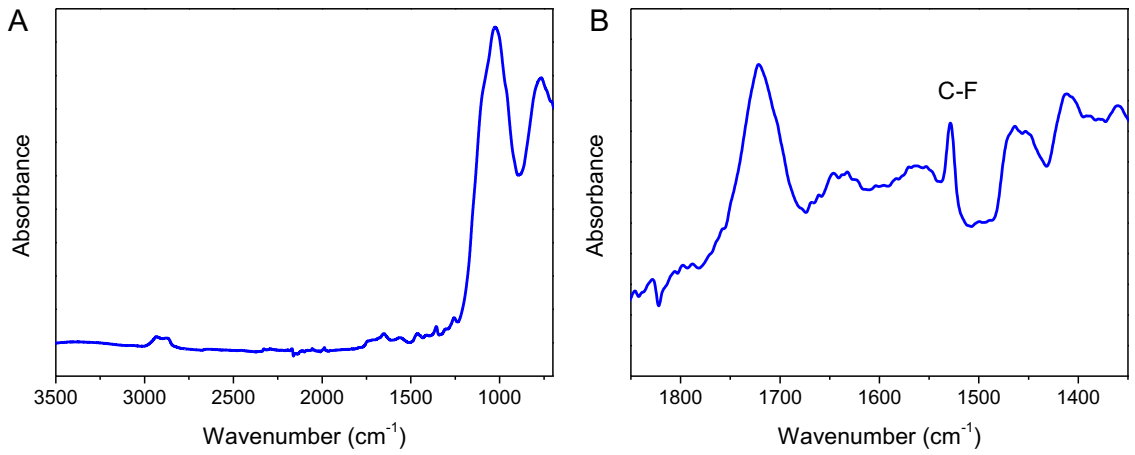


**Fig. S4**. ATR-FTIR spectrum of A) a THCpSi film exclusively internally functionalised with PFP; B) shows a zoom-in in the spectral range of 1850-1325 $cm^{-1}$. The signature peak of PFP arises at 1520 $cm^{-1}$.

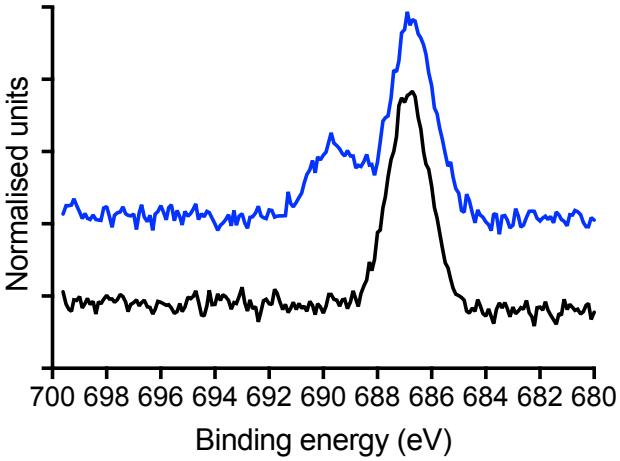


**Fig S5**. XPS high resolution XPS F 1s spectra for thermally hydrosilylated THCpSi (black line) and internally functionalised THCpSi with PFP. The additional peak observed at binding energy of 689.5 eV after PFP functionalisation corresponds to C-F, whereas the peak at 687 eV corresponds to ionic F. The latter is detected on all HF-etched pSi surfaces.

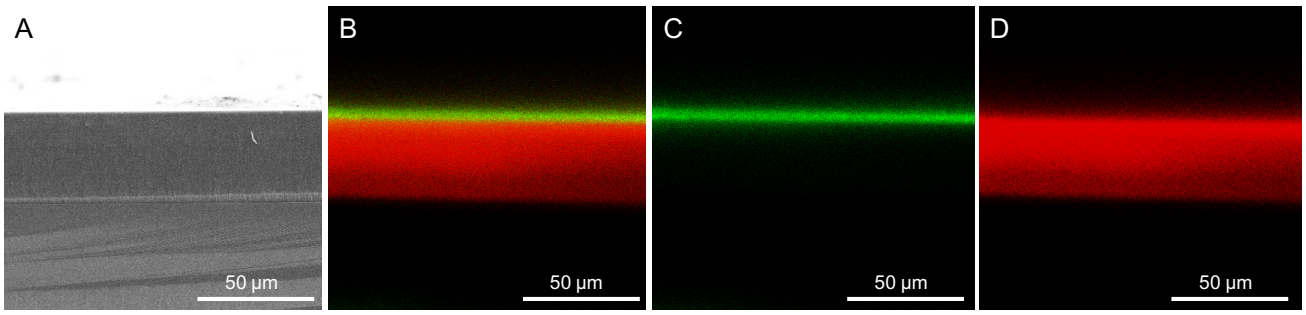


**Fig. S6**. Cross-sectional images of pSi films. (A) SEM image, showing a nanoporous layer of freshly-etched pSi with a thickness of approximately 35 µm. Cross-sectional views by fluorescence confocal microscopy of a differentially functionalised THCpSi layer collected in the (B) green and far-red channels (simultaneous laser excitation at 485 and 640 nm); (C) green channel (excitation at 485 nm); and (D) far-red channel (excitation at 640 nm).