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Preparation and characterisation of vertically aligned single-walled carbon nanotube arrays on porous silicon

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ABSTRACT

Vertically aligning carbon nanotubes (VACNTs) onto 2D porous materials is advantageous for many conceivable electronic applications but also for investigating the unique water transport properties of CNTs and the molecular separation of molecules during fluid transport through their inner shell. Here we report a wet chemical technique to produce vertically-aligned single walled CNT arrays on porous silicon (pSi). The nanotubes were first acid treated to produce carboxylic acid functionalities on the single-walled CNT. The carboxy-functional nanotubes were then covalently immobilised on a pSi surface that had been either ozone treated or silanated with aminopropyl triethoxysilane (APTES). The VACNT surfaces were analysed with atomic force microscopy (AFM), confocal Raman spectral imaging and Fourier transform infrared (FTIR) spectroscopy. Dense arrays of VACNTs were observed with the obtained CNT orientation and surface coverage depending upon attachment method and attachment reaction time.

Keywords: Single-walled carbon nanotubes; porous silicon; vertically aligned carbon nanotubes; atomic force microscopy

1. INTRODUCTION

Since 1991, carbon nanotubes (CNTs) have attracted significant attention due to their unusual mechanical and electrical properties.¹⁻⁷ Interest has recently been shifted toward investigating the flow of fluids through the inner shell of CNTs for purposes of investigating flux with various fluids or as size-based chemical or biological separation devices.⁸⁻¹⁰ CNTs are advantageous for these purposes over other carbon based nanopores such as chemical vapour deposition (CVD) grown nanotubules based on porous alumina templates¹¹ because the smoothness of the inner walls of CNTs leads to an almost frictionless transport of some fluids.^{12, 13} At the same time, the size of CNTs is much smaller and more controllable leading to both a higher flux and selectivity.

However, experimentally producing CNT arrays suitable for the study of fluid transport has proven to be difficult. The generally adopted approach is to grow an aligned array of CNTs using CVD, fill in the gaps between the CNTs with polymer (or similar) and finally remove the substrate under the CNTs as well as the tops of the CNTs via an etching technique. This process has been used to create multi-wall carbon nanotube (MWCNT) and double wall carbon nanotube (DWCNT) arrays^{14, 15} to investigate flow of gases⁹, liquids⁸ and for ionic separation.¹⁰ The limitations of this process are the incomplete removal of catalyst particles which inhibits flow, the use of large radius MWCNT and DWCNTs limiting size-based separation, and the lack of support of the CNT membrane after removal of the substrate, which compromises the stability of the system.

A simple method to produce vertically aligned single-walled carbon nanotubes (VASWCNTs) has recently been developed where pristine SWCNTs are treated with concentrated acid to both shorten the nanotubes and produce carboxylic functionalities on the ends.¹⁶ The carboxylic acid groups are then reacted with either a hydroxylated surface or an aminopropyl triethoxysilane (APTES) layer to form VASWCNT arrays.¹⁷⁻¹⁹ Arrays such as these could be advantageous over the CVD-grown CNT arrays in fluid transport/separation experiments since there is no blocking from unremoved catalyst because catalyst particles are removed during the acid treatment and because SWCNTs synthesised by arc-discharge have a smaller diameter than those produced by CVD. Such experiments will require the substrate (commonly silicon) to either be removed by etching¹⁴ or be porous.

Porous silicon (pSi) is produced through the chemical, photochemical or electrochemical etching of flat, crystalline silicon with fluoride solutions.²⁰⁻²² The pores formed can be in a range of tuneable sizes from micropores (<5nm) to mesopores (5-50nm) to macropores (>50nm) with a depth depending on the etching time.²³ After etching in hydrofluoric acid (HF) the pSi surface is left hydrogen terminated,²⁴ which can be further reacted to perform a range of surface chemistries.²² Porous silicon membranes, open at both ends, can be generated by either extending the etching time until the whole thickness of the wafer is etched²⁵ or by using the 'lift off' technique²⁶ which results in porous membrane detachment from the silicon substrate.²⁷

Here, SWCNTs will be chemically attached to pSi using various methods similar to techniques that have previously been used to successfully create VASWCNTs arrays on flat silicon. The suitability of each created SWCNT array as a potential substrate for investigation of fluid flow and molecular separation will be discussed based upon the orientation and density of chemically attached SWCNTs.

2. EXPERIMENTAL

2.1 pSi formation

Porous silicon substrates were prepared from p-type (boron doped) silicon wafers with (100) orientation and a resistivity of 3-6 Ω cm (Silicon Quest International). The silicon wafers were etched in a custom made Teflon cell with an etching area of 1.767 cm². Prior to etching, the wafer was washed with methanol, acetone and dichloromethane (DCM) and dried under a stream of nitrogen. Etching was carried out at a constant current of 66mA (supplied by a Keithley 2425 source meter) for 120 seconds in a solution of 1:1 (v/v) 48 % aqueous hydrofluoric acid (HF, Merck)/ethanol (100 % undenatured, Chem-Supply). The hydrogen terminated etched pSi substrate was then rinsed consecutively with methanol, acetone and DCM then dried under a stream of nitrogen.

2.2 Hydroxylation of the pSi

The hydrogen-terminated freshly etched pSi substrate was hydroxylated using two different methods: ozone and wet chemical treatment. Ozone hydroxylation was carried out by exposing freshly etched pSi to ozone using a Fischer ozone generator with the current set at 1.2 A and an O₃ flow rate of 3.2 g hr⁻¹ for 10 to 60 min. Wet chemical hydroxylation was carried out by adding a freshly etched pSi wafer to piranha solution, 3:1 (v/v) H₂SO₄ (98 %, Labscan Asia Co. Ltd.):H₂O₂ (30 %, Chem-Supply), for 20 to 60 min at 80 °C. The pSi substrate was then washed with MilliQ water and dried under a stream of nitrogen or further reacted with a solution of 1:1:5 (v/v) NH₄OH (30 %, Sigma-Aldrich):H₂O₂:MilliQ water for 5 min at 80 °C then washed with MilliQ water and dried under a stream of nitrogen.

2.3 SWCNT cutting

P2-SWCNTs (Low Functionality; purified) were purchased from Carbon Solutions Inc., California, USA. The nanotubes are produced via electric arc discharge using Ni-Y catalysts and have a carbonaceous purity of 70-90 % with minimal functionality as determined by solution-phase near-IR spectroscopy²⁸. P2-SWCNTs (20mg) were shortened/cut by adding to 20 mL of 3:1 (v/v) solution of concentrated H₂SO₄ (98 %):HNO₃(70 %) in an Elma S30 H ultrasonic bath kept at 0 °C for 8 h by periodically adding ice. The cutting was stopped after 8 h by adding a 50 fold excess of MilliQ water. The shortened SWCNTs were then filtered under vacuum through a 0.45 μ m PTFE (polytetrafluoroethylene) filter (Adelab Scientific, Thebarton, South Australia). The filtered carboxylated SWCNTs were further washed with MilliQ water until a pH of between 5 and 7 was obtained then placed to dry in an oven at 80°C for 12 hours.

2.4 Direct ester attachment of SWCNTs to pSi

The dried carboxylated SWCNTs were suspended in 100 mL of dimethyl sulfoxide (DMSO, 99.9 %, ACS Spectrophotometric Grade, Sigma-Aldrich) along with 20 mg of the activating agent N,N'-dicyclohexylcarbodiimide (DCC, 99 %, Aldrich) creating a 0.2 mg mL⁻¹ SWCNT suspension and sonicated for 4 h prior to use.

2 mL of activated shortened SWCNT suspension (0.2 mg mL⁻¹) was then added to a round-bottomed flask containing a hydroxylated pSi substrate, inside a nitrogen filled glove box. The flasks were then stoppered and wrapped in parafilm and fibreglass tape to ensure a good seal before being taken out of the glove box and placed into an oven at 80 °C for varying amounts of time (2 to 24 h). The substrates were then rinsed thoroughly in acetone to remove any unbound reagents and dried under a stream of nitrogen.

2.5 Phosphorus pentasulfide attachment of SWCNT to pSi

A pSi substrate, hydroxylated by 10 min ozone treatment, was added to a pre-sonicated (5 min) solution of cut SWCNTs (1 mg), 1 % (v/v) pyridine, and 1 mg of phosphorus pentasulfide in 10 mL of dried toluene. The substrate and solution were then sonicated for 20 mins at 50°C. The substrate was then removed, washed with dichloromethane (DCM) and acetone and dried under a stream of nitrogen.

2.6 Aminopropyl triethoxysilane attachment of SWCNTs to pSi

A pSi substrate, hydroxylated by 10 min ozone treatment, was placed into a 0.5 % solution of 3-aminopropyl triethoxysilane (APTES, 99 %, Sigma–Aldrich) in anhydrous toluene for 5 min. The substrate was then removed from solution, washed by rinsing sequentially in chloroform, acetone and water and dried under a stream of nitrogen. The substrate was then placed into approximately 3 mL of the 0.2 mg mL⁻¹ SWCNT, 0.2 mg mL⁻¹ DCC in DMSO solution that had been pre-sonicated for 4 h. The wafer was allowed to sit in the SWCNT solution for times varying from 5 min to 24 h until, then removed and washed thoroughly with acetone and dried under a stream of nitrogen.

2.7 Atomic force microscopy (AFM)

AFM tapping mode images were taken in ambient conditions with a multimode head and a Nanoscope IV controller (Digital Instruments, Veeco, Santa Barbara). Silicon cantilevers (Mikromasch) with fundamental resonance frequency of between 200-400 kHz were used. Images were obtained using a scan rate of 1 Hz with the parameters of set point, amplitude and feedback control optimised manually for each sample. The images presented have been flattened using Nanoscope 6 software.

2.8 Confocal Raman spectral imaging

Confocal Raman spectra were recorded on a Witec alpha 300 Confocal Raman Spectrometer fitted with a 532nm laser (60 mW) using both a x100 (0.9 numerical aperture (NA), working distance (WD) 0.23 mm) and a x40 (0.6 NA WD 3.7 to 2.7 mm) objective. The presented spectra were taken as an average of 2 scans over a collection time of 50 sec. Confocal images were completed by taking 100 lines of 100 spectra with an average integration time of 0.1 sec. The Confocal Raman images represent the relative height of the G-band (1530-1630 cm⁻¹) for each individual spectrum. The experiments were carried out using Witec Control 1.42 software and the analysis was completed using Witec project 1.90 software.

2.9 Fourier transform infrared spectroscopy

FTIR spectra were recorded on a Nicolet Avater 370MCT spectrometer (Thermo Electron Corporation). The spectrometer was fitted with a transmission accessory, all spectra were recorded over a range of 650-4000 cm⁻¹ at a resolution of 2cm⁻¹ as an average of 64 scans and analysed using OMNIC version 7.3 software. All FTIR spectra were collected with a background of clean flat/non-functionilised silicon wafer of the same type as the samples.

3. RESULTS AND DISCUSSION

3.1 Preparation and hydroxylation of pSi

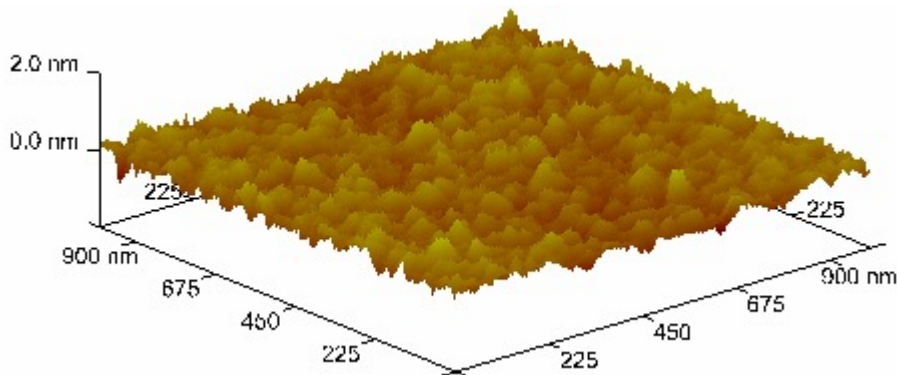
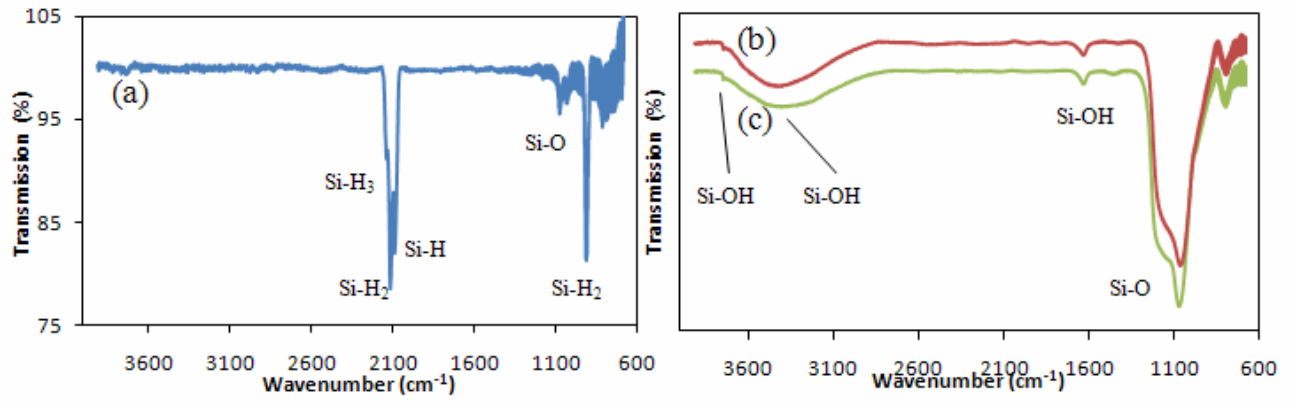


Fig. 1: AFM of freshly etched pSi. Etching conditions: 1:1 (v/v) HF/ethanol, 66mA, 120 sec.



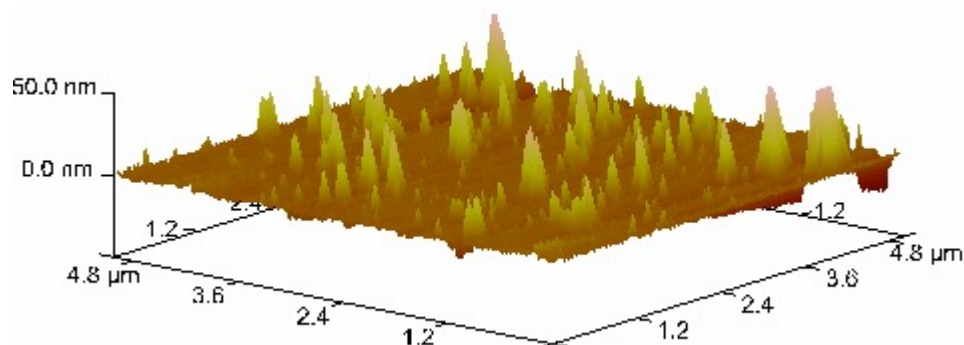


Fig. 3: AFM image of SWCNTs chemically attached to pSi following the direct ester attachment method.

The calculated SWCNT coverage of SWCNT on pSi in Fig. 3 is 7 % compared to 22 % for the same attachment on flat Si. This reduction in coverage is thought to be due to the formation of geminal silyl esters on the pSi substrate. Silyl esters are susceptible to degradation because the bond can be cleaved by attack at either the carbonyl or the silicon atom.⁴⁰ Degradation of silyl esters has been found to increase depending upon the environment of the silicon. Hydroxylated flat silicon (100) involves one silicon atom with one hydroxyl group. Porous silicon on the other hand can have 1, 2 or 3 hydrogens on the surface silicon atoms after etching which means it could have 1 to 3 hydroxyl groups on each surface silicon atom after hydroxylation.⁴¹ If a silicon atom forms an ester linkage with two or more SWCNTs (known as a geminal ester) the degradation is found to be much faster because of the loss of steric and electronic stability.^{42,43}

3.3 Phosphorous pentasulfide mediated attachment

The attachment of SWCNTs using the versatile catalyst phosphorous pentasulfide has recently been achieved on flat silicon to produce vertically aligned arrays.⁴⁴ Fig. 4 shows the results of attaching nanotubes using phosphorous pentasulfide with hydroxylated pSi (10 min ozone). The 3D AFM image (Fig. 4 (a)) appears similar to Fig. 3 where there are VASWCNTs of 20 to 50 nm in height. However the top down view (Fig. 4 (b)) reveals that there is a large number of SWCNTs lying down. This orientation was consistently observed throughout a number of P_4S_{10} mediated attachments but never observed with the direct ester attachment. We attribute this effect to the different mechanism of attachment involving the conversion of surface hydroxyl groups to thiols.⁴⁴ On the pSi surface, the germinal hydroxyl groups are converted to geminal thiol groups (in the presence of P_4S_{10}) these newly formed thiols may oxidise to form a disulfide bond. These bonds render the surface more hydrophobic which might encourage adsorption of the SWCNTs sidewalls, resulting in side-on attachment.

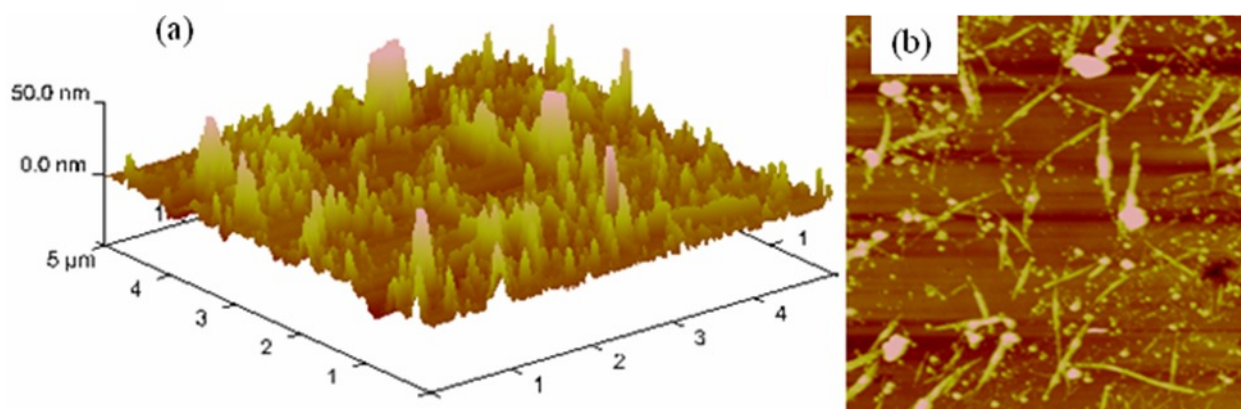
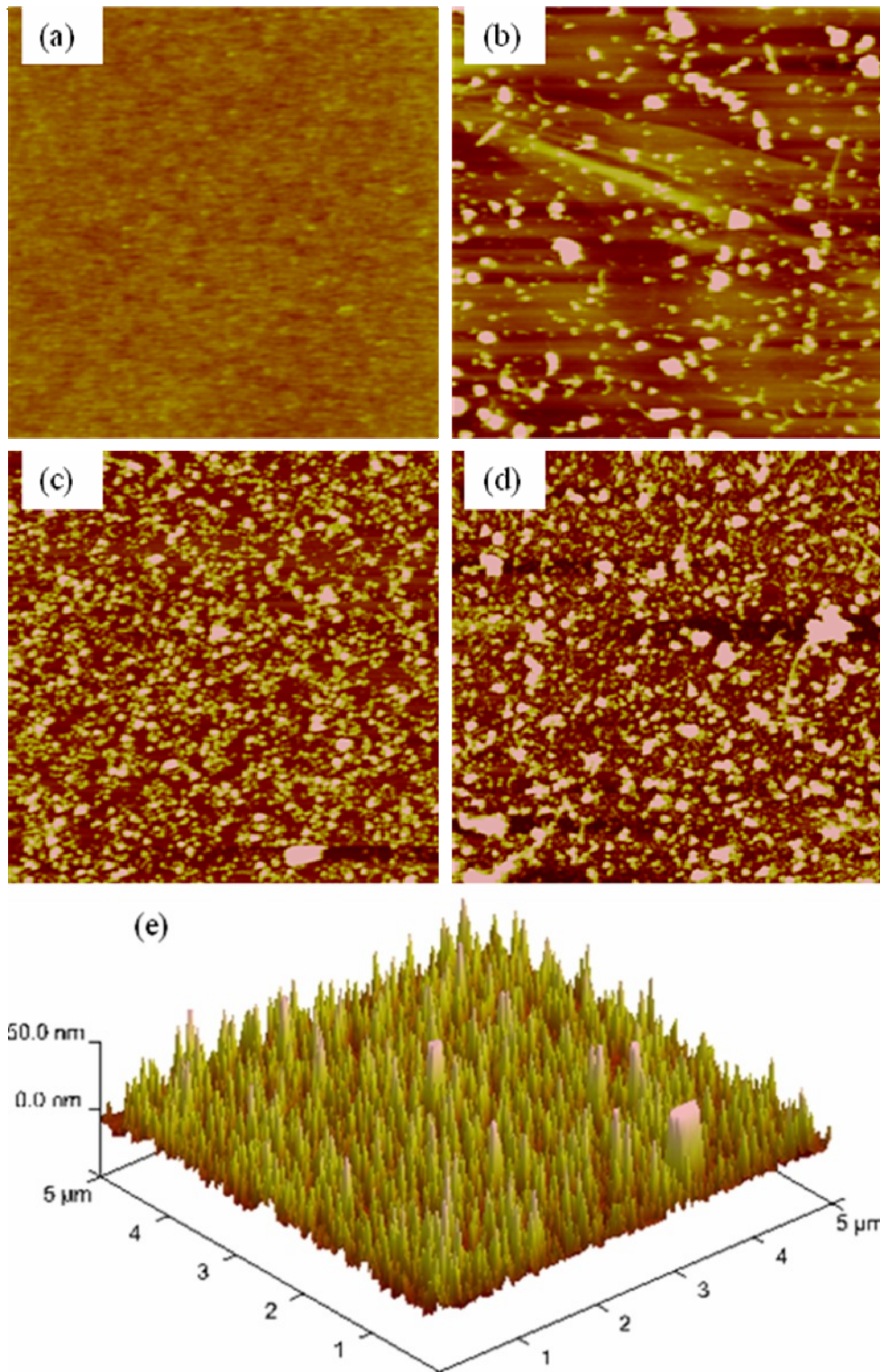
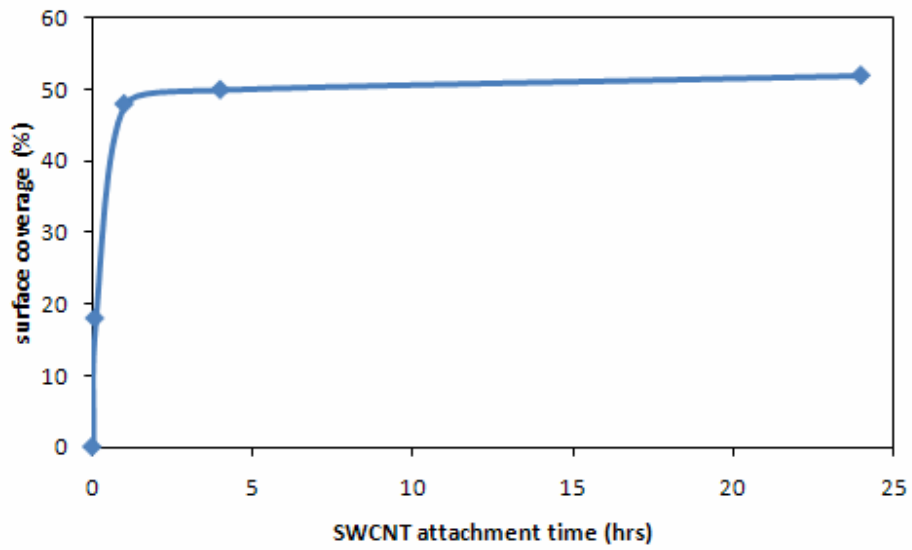
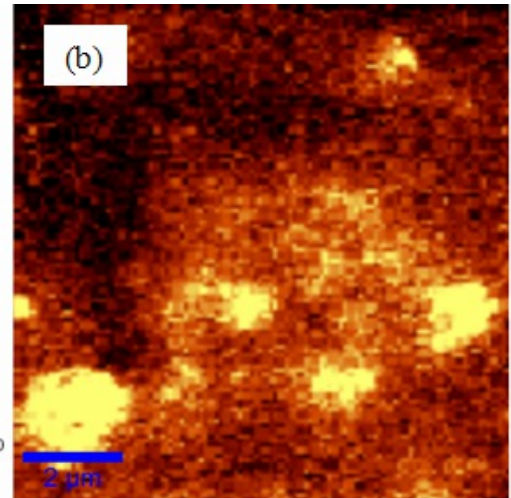
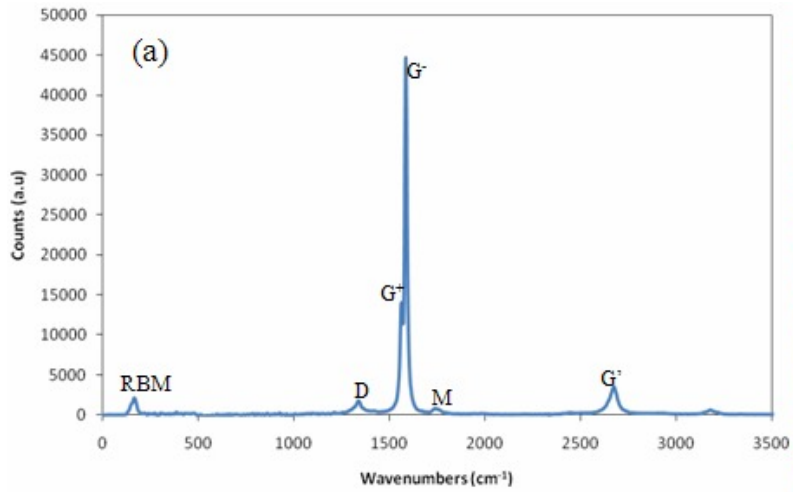
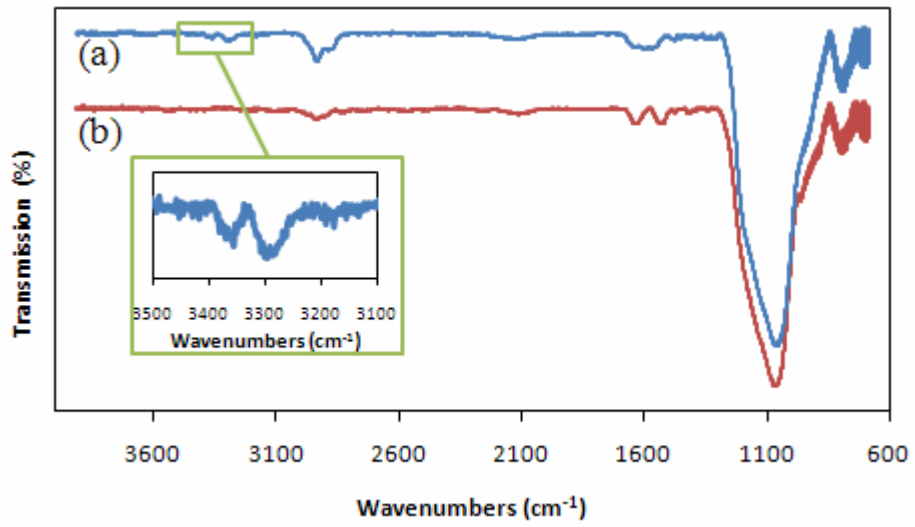


Fig. 4: AFM images ($5 \times 5 \mu\text{m}^2$) of (a) 3D and (b) top view AFM image ($5 \times 5 \mu\text{m}^2$) of covalently attached SWCNTs on pSi using using phosphorus pentasulfide as a catalyst.







4. CONCLUSIONS

Vertically-aligned SWCNTs (VACNTs) have successfully been covalently attached to pSi via three different attachment protocols. Namely, direct ester attachment, phosphorus pentasulfide mediated (thioester attachment), and to an APTES monolayer (amide attachment). Direct ester attachment produces well oriented VACNTs but with low density, P_4S_{10} mediated produces a higher density but loss of vertical-alignment. The attachment to the APTES monolayer on pSi produces high density and well orientated VACNTs. These attachment protocols could potentially be used in the formation of VACNT membranes for the study of fluid transport or molecular separations.

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