

**Long Lifetime, Superhydrophobic, Free-standing
Carbon Infiltrated Vertically Aligned Carbon Nanotube Structures**

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Abstract

Long lifetime, free-standing, superhydrophobic, carbon infiltrated vertically aligned carbon nanotube structures (ct-VACNT) are prepared by VLS assisted VACNT growth on photolithographic patterned catalyst wafers, followed by a carbon infiltration process creating c-VACNT precursor structures (made from a nanoporous carbon sponge material) which are subsequently released from the catalyst wafers, surface roughened on their top and bottom surface and then conformally overcoated with a few nm thick hydrophobic thin film of a hydrophobic amorphous fluoropolymer, thus resulting in free-standing superhydrophobic ct-VACNT structures. Longevity testing of the hydrophobic overcoating shows that the addition of a customized surface roughening step (especially in the form of low-pressure O₂ plasma-assisted surface burning of the nanocarbon sponge material) for the bottom and top surfaces is key to extending the hydrophobic lifetime of such ct-VACNT structures from a few weeks to over a year.

These long lifetime ct-VACNT structures can now be used to develop novel fluid processing devices for a range of industrial and medical fluid processing applications requiring gas transfer into and/or out of aqueous liquids. Such novel fluid reactor devices are enabled by application-specific optimized components made from these novel nano-to macro ct-VACNT structures, for example in the form of Fluid channel Array Bricks (FABs).

Keywords:

ct-VACNT structures, c-VACNT precursors, carbon nanotubes, superhydrophobic, contact angle, O₂ plasma surface roughening

1. Introduction

Carbon nanotubes (CNTs) have been the focus of research in the last few decades due to their unique electronic and mechanical properties¹. Their properties have been utilized primarily for incremental improvements in various applications such as solar cells, electronic components, supercapacitors, as well as in composite polymer materials²⁻⁴. Synthesis of CNTs can be achieved using arc discharge, laser ablation, high-pressure carbon monoxide disproportionation (Hipco), and chemical vapor deposition (CVD)^{5,6}. In a CVD process, thermal decomposition of a hydrocarbon vapor on a catalyst substrate has been used to produce vertically aligned carbon nanotubes (VACNT)^{5,7-9}.

Recently, carbon infiltrated VACNT structures have been proposed for MEMs^{10,11} and as all carbon watch springs. Such structures are also being explored for gas transfer applications for aqueous fluids, like blood oxygenation, and as a possible replacement for hollow fiber devices for a range of other applications^{12,13}. However, to date little is known about the longevity of related gas transfer rates into and out of aqueous fluids for such devices. Research in this matter is necessary to justify related future medical and/or industrial application developments¹⁴. Ideally, low-cost, volume scalable production methods are discovered and validated to prove that hydrophobic ct-VACNT structures can be made with over one-year longevity. If such a goal can be accomplished, then VACNTs in the form of ct-VACNT structures could become key application enable components that potentially can enable a whole new product spectrum of hollow fiber replacing devices, not just a small percentage product additive, as CNTs have found typical commercial applications thus far.

In this work, we investigate FABs that are special forms of carbon infiltrated VACNT structures. Such FABs can be designed to be application-specific, key enabling

components, for example for fluid-gas exchange for medical or industrial applications. When needed, we surface modify these components locally to become superhydrophobic so that such modified FABs can potentially replace hollow fibers in selective medical or fluid exchange processing applications^{15,16}. To determine the potential of these hydrophobic FABs, extended hydrophobicity lifetime testing was performed to validate its stability for extended use applications. Through iterative process improvements, the resulting contact angle and the lifetime of these hydrophobic FAB surface treatments have been extended to over one year.

2. Materials and Methods

2.1 Materials

99.99 % Hydrogen, and Nitrogen gases were used as well as Research and UHP grade Ethylene for the CNT growth and carbon infiltration process steps respectively. 1% Teflon AF 2400 dissolved in Fluorinert FC-40 were used as sold by Chemours for the conformal polymer film coating process step. 99.9% pure SiO₂, Al₂O₃, and Fe granulate/pellets were used for the ebeam deposited multilayer catalyst thin films process steps. 4” diameter Si wafers were used as catalyst wafer starting substrates.

2.2 Experimental

2.2.1 Patterned catalyst substrates manufacturing

Photolithographic patterned single-sided catalyst substrates, which include a 20 nm SiO₂ film, a 10 nm Al₂O₃ film, and a 0.8 nm Fe film, all deposited in series with an e-beam deposition system, were loaded into a horizontal quartz process tube of an EasyTube® 3000 system (see SI Fig. 1) with an ID ≈ 5”. The UV mask pattern used for the photolithography process controls the cross-sectional shape of the resulting

standalone released c-VACNT structures and therefore their application-specific properties and performance.

2.2.2 VACNT growth and carbon infiltration steps for manufacturing c-VACNT precursors

These catalyst wafers were exposed to a mixture of process gas precursors having the flow rates of $N_2/H_2/O_2/C_2H_4 = 2769/3194/2/2396$ sccm or $Ar/H_2/Air/C_2H_4 = 2769/3194/10/2396$ sccm during the 60-90 minutes vertical aligned carbon nanotube growth step at 750 °C and atmospheric process conditions. For these samples, a substantially conformal coating deposition process step, also at atmospheric pressure, was accomplished at a process temperature of 900 °C and $H_2/C_2H_4 = 12,000/4,000$ sccm, for 30-90 minutes depending on the desired final structural density of the application dependent targeted c-VACNT structures (see SI Fig. 2). For maximum repeatability research-grade, C_2H_4 was used for the VACNT growth step, and for economic reasons UHP grade C_2H_4 was used for the carbon infiltration process.

This carbon infiltration process substantially increases the thickness of each carbon nanotube (CNT) by $2T$ with a conformal thin film having a thickness T , where T ranges from a few nm to tens of nm, depending on the carbon infiltration time. This substantially conformal carbon infiltration process therefore locally spot welds two neighboring CNTs together (see Fig. 1a) where they nearly touch each other (i.e. the contact distance d is $d < 2T$), thus transforming a structurally weak vertically aligned CNT array held together by weak Van Der Waals forces into an open-pore cellular network material having a bi-continuous tortuous phase structure (see Fig. 1b), i.e. a novel nanocarbon sponge-like structure where individual CNTs are locally carbon-spot-welded, approximately every 200- 500 nm along their length.

This results in a novel nanocarbon structure with vast superior mechanical strength that survives even an acetone soaking and subsequent acetone evaporation, i.e. a wetted c-VACNT structure drying process step, without structural collapse or three-dimensional geometrical change. This structural strength of the c-VACNT material enables now also surface modifications of all the internal nanocarbon sponge surfaces with manufacturing processes that utilize one or more liquids exposures and their removal thereafter. Moreover, it enables applications that expose at least some localized surfaces of these c-VACNT structures to hydrophobic and hydrophilic liquids over extended periods.

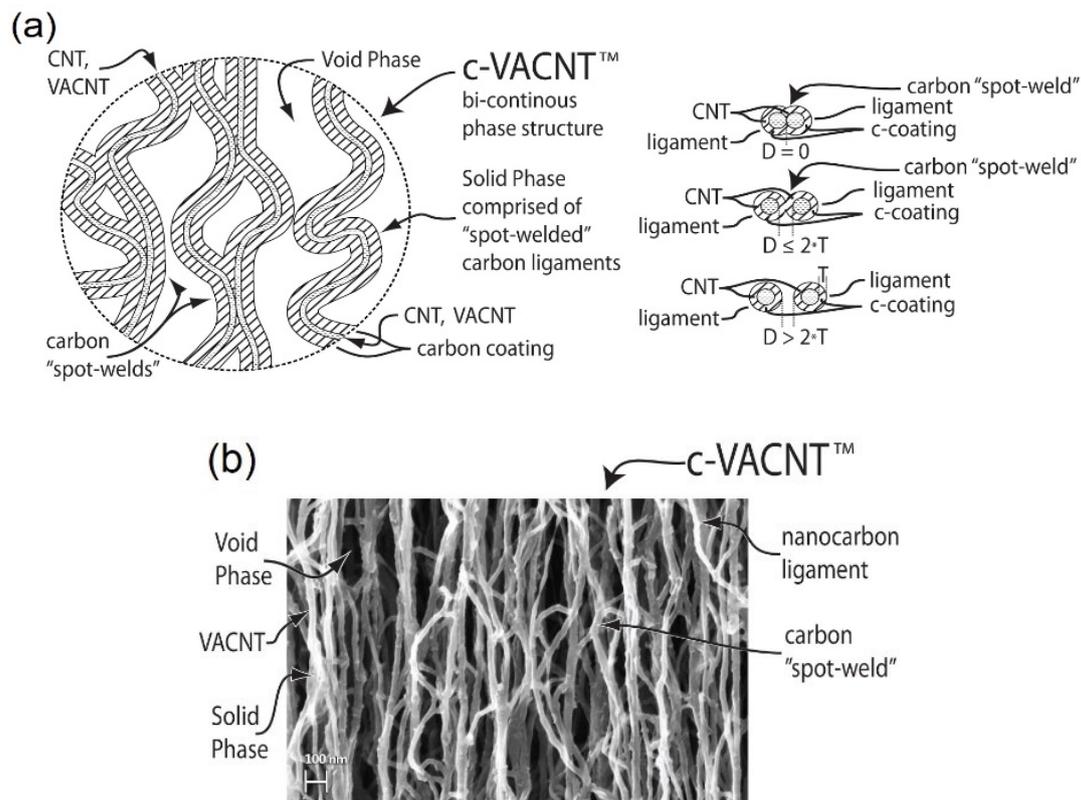


Fig. 1: Carbon infiltration process of VACNT forest with conformal carbon film (a) the effect of the tube spacing (D) on the formation of locally spot-welded VACNTs, (b) SEM images of carbon infiltrated vertically aligned CNT array forming an open-pore cellular network material having a bi-continuous tortuous phase structure.

Since the conformal carbon coating process coats all surfaces, it also conformally coats the catalyst wafers surface between all CNTs endings in contact with the growth wafers

and therefore covers all the space between the CNTs and even all through holes (for example $\geq 50 \mu\text{m}$ diameter through holes) or gaps between the VACNT structures. This bottom carbon film layer that connects mechanically at parts in contact with the catalyst wafer surface, i.e., all CNT bottom endings, is also called herein a floor layer (see Fig. 2a and SI Fig. 3). If the growth Si wafer is polished, this floor layer results in a mirror-like shiny reflective surface with very little roughness.

Typically, up to 2-3 mm tall c-VACNT precursor structures can be substantially conformally coated top to bottom with a small thickness gradient versus the bottom (near the growth substrate) with only an $\approx 10\text{-}20 \mu\text{m}$ thick “crust layer” at the top (see Fig. 2b). The top crust CNT film is a dense, approximately horizontal oriented CNT layer that is the result of the initial horizontal intertwined growth of the CNTs until their tips sufficiently mechanically interconnect to form a macroscopic nonwoven felt like carbon nanotube carpet. Once this carpet is dense enough that it mechanical links all the tips of the CNTs together into a macroscopic structure, which then gets lifted by the continuous growing CNT’s that then together pushes it up, i.e., away from the growth substrate surface thus resulting in the typical corkscrew wavy VACNT structure that is also visible in Fig. 1b.

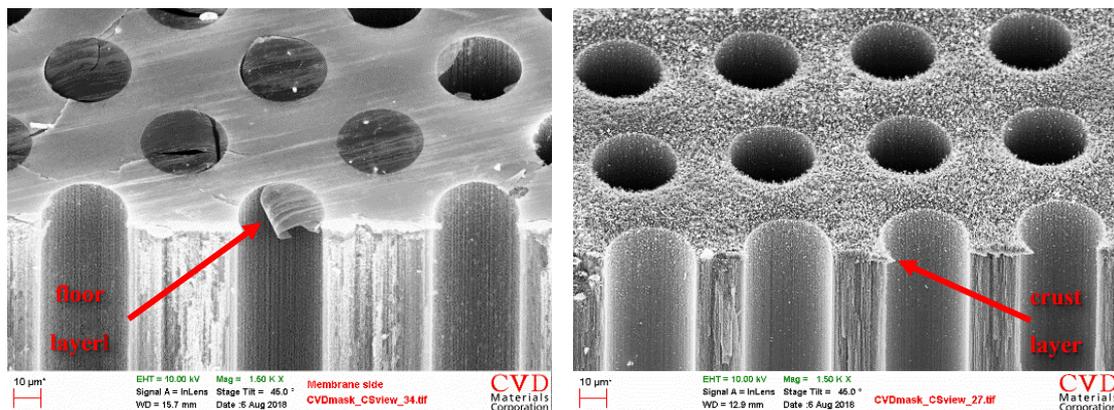


Fig. 2.: SEM images of the bottom (a) and top (b) side of native c-VACNT structures after separation from its growth wafer; (a), the left image, shows that even large area openings (fluid channels) are covered with thin carbon film after the carbon infiltration step, and (b), the right image, shows that the top side has a thin denser crust layer of $\approx 10\text{-}20 \mu\text{m}$ thickness.

2.2.3 VACNT substrate separation

These c-VACNT precursor structures then were separated from their growth substrate with a liquid processing step. We used a low-tech, vibratory shaker table that holds in a sealed container a wafer covered with c-VACNT precursors (see SI Fig. 2) submerged in a separation liquid (2-10% HF or mixture of HF and HCl diluted in water). The mechanical vibration speeds up the separation process. The HF (optional HCl) solution etches primarily the SiO₂ (Al₂O₃) layer underneath the c-VACNT precursor structures, which then allows them to separate from the Si growth wafer. This allows hands-free and industrially scalable separation of c-VACNT precursors from their growth substrate resulting in the defect-free release of manufactured c-VACNT structures, irrespective of their possible fragile structural cross-sectional designs. This separation process steps typically takes 15-120 minutes (or overnight when not agitated), depending on the height and width of the c-VACNT structures and the gap between neighboring structures. It also depends on the strength of the HF/HCl concentration of the separation liquid.

After the separation process, when these c-VACNT structures have small diameter through holes (for example fluid channels with diameters of $\leq 50 \mu\text{m}$), some of them typically have a thin carbon floor layer (membrane) that covers at least a substantial area of them, thus fully or at least partially blocking fluid passage through these fluid channels (see Fig. 2a). For many applications, the device performance of such c-VACNT structures is improved if all these full or partial carbon film membranes get removed from the respective fluid channels before their usage, i.e., all respective fluid channels are fully open, and no such carbon membrane pieces get flushed out of them over time when fluid passes through such them.

The image SI Fig. 3 shows an example of a range of free-standing c-VACNT structures labeled ST1-ST12 for their different shape and/or fluid channel perforation patterns, that were separated from the c-VACNT precursor wafer shown in SI Fig. 2.

2.2.4 c-VACNT structure surface roughening

2.2.4.1 Experiment 1:

In the first series of experiments, we did not use any surface roughening process and moved to the next step, i.e., 2.2.5, without further processing the released c-VACNT structures.

2.3.4.2 Experiment 2:

In the second series of experiments, we used a commercial vibratory polisher with fumed Al₂O₃ or SiO₂ as polishing media to remove the bottom carbon floor layer and the top crust layer from the released c-VACNT structures. Slight weights were placed on top of the c-VACNT structures to prevent them from floating off the polishing felt. We also subsequently washed the polished parts with diluted HF or HCl to remove most of the penetrated polishing particles.

2.2.4.3 Experiment 3:

In the third series of experiments, we used a commercially available plasma descumming system (YES CV100PZ) with a robotic cassette to utilize the loading mechanism that was originally designed to remove remaining polymer films from wafers after a photolithographic stripping process step. To be able to utilize the available robotic loading system we designed and build a custom tooling (graphite plate with cut-outs) that was placed on top of a Si wafer and that therefore allowed O₂ plasma treatment of one surface of the c-VACNT structures at the time with this plasma system. For this 3rd experiment, all c-VACNT structures were exposed first on their top side

with a 1st O₂ plasma recipe, then flipped over, and subsequently, their bottom side got exposed to a 2nd O₂ plasma recipe.

The purpose of this double-sided O₂ plasma treatment was to suitably surface roughen the different top and bottom sides of these c-VACNT structures to 1) remove all the floor layers with an easily executable and mass-producible process step, 2) roughen the ultrasmooth bottom side of the c-VANT structures by removing all the remaining floor layer connecting the bottom CNT endings, 3) remove the top densified surface layer visible in Fig. 2b, and 4) to transform the flat surface with through holes into conical funnels with a round to rectangular shape conversion for a lower pressure drop of fluid passing through the respective fluid channel perforations. Given the different carbon density at the top and bottom surface and slightly different carbon infiltration thickness, different plasma process recipes for the top and bottom layer of the c-VACNT structures were used to make the top and bottom size more equal in surface roughness and conical entrance shape. For the smother bottom side, we used a *1-minute* plasma treatment process step at 90 °C and for the rougher and denser top side of the c-VACNT structures, a *10-minute* treatment step at 150 °C was used which resulted in a similar 3-D funnel-shaped top and bottom surface morphology shown in Fig. 3 from the starting original shape shown in Fig. 2. Low pressure (≈ 2 Torr) was used for both process steps.

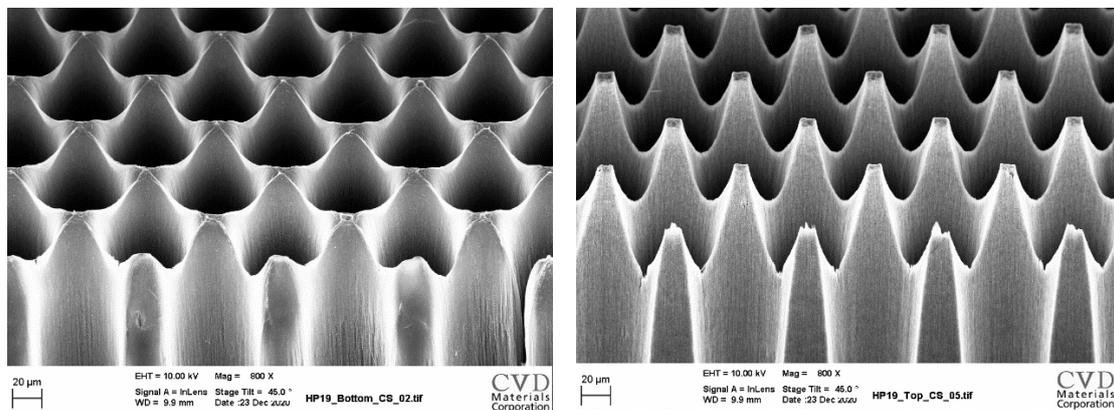


Fig. 3.: SEM images of the bottom (a) and top (b) side of separated O₂ plasma surface treated c-VACNT structures; the left image (a), shows the bottom surface with now fully open fluid channels with a conical round to rectangular funnel transitions, and the right image (b) shows the top surface, also with a conical round to rectangular funnel transitions.

2.2.5 Hydrophobic coating application

2.2.5.1 Cleaning:

First, c-VACNT structures were baked in an H₂ atmosphere for 15 min at 900 °C and then cooled to room temperature using a FirstNano EasyTube 2000 system. This step was done to maximize cleaning of all the internal surfaces of the porous sponge-like c-VACNT structures to remove any leftover hydrocarbons and other adsorbed volatiles like water vapor, and/or acids from the c-VACNT precursor growth, subsequent separation, and/or surface roughening process steps.

2.2.5.2 Liquid hydrophilic surface film deposition:

Then a conformal hydrophobic coating was applied to free-standing c-VACNT structures by 1) first soaking them in a commercial available Teflon® AF 2400 solution that has been heated to ≈ 50 °C to lower the solution's viscosity, thus shortening the 100% fluid penetration time into the nanoporous sponge material to ≤ 5 min and resulting in less fluid drag out upon removal of the soaked structures, 2) then removing these diluted polymer liquid-filled c-VACNT structures from the solution and very slowly air drying them overnight in a fume hood to remove most of the remaining solvent. This allowed the dissolved solids to form a continuous conformal film at the nearest surface, thus conformally coating all the surface of the nanocarbon sponge of which the c-VACNT structure is comprised. Then in a backout process step 3) any remaining solvent and possible any lingering PFA residuals inside the nanoporous c-VACNT structures were removed by heating them slowly under air in an oven to a maximum baking temperature of 290 °C, holding this temperature for about 5 - 15

minutes to further anneal the polymer film, and then cooling them slowly to $< 100\text{ }^{\circ}\text{C}$, thus resulting in the targeted free-standing ct-VACNT structures.

The total bakeout process takes less than *2.5 hours* and allows many c-VACNT structures to be processed in parallel. We used the same FN 2000 system for both this bakeout step and the prior H₂ backout step. The maximum baking temperature was chosen to be at least about 10 °C above the boiling point of the solvent and 5°C above the glass transition temperature point T_g of the polymer ($T_g = 240\text{ }^{\circ}\text{C}$ for Teflon AF 2400), but less than the thermal decomposition temperature of the chosen polymer material ($> 310\text{ }^{\circ}\text{C}$ for short time exposure). For the samples tested with Teflon AF 2400 coating, we chose a maximum bakeout temperature of $290\text{ }^{\circ}\text{C}$ to maximize PFA removal rates. This allowed removing any last trace of solvents, annealing and densifying the polymer film, and smoothing any hills and valleys of the polymer film formed during the drying process step, thus ensuring maximum conformally overcoating of even the exposed CNT endings. This custom-developed liquid polymer deposition process permits the polymer to spread uniformly over all surfaces of the nanoporous sponge material of which the c-VACNT structure is comprised off, irrespective of the height and porosity of the structure and its varying pore size through the structure and it also conformally covers the CNT tip endings.

2.3 Characterization

2.3.1 Imaging: Scanning electron and digital microscopy was used to collect images of all grown c-VACNT and ct-VACNT structures and their cross-sections.

2.3.2 Weight gains: A digital scale with 0.01 mg resolution was used for weight gain analysis of VACNT structures during the carbon infiltration step and the hydrophilic

coating application steps. For the surface area analysis, an average spacing of 80 nm between neighboring CNTs and an average diameter of 10 nm for multiwall CNTs was used, which, in conjunction with the weight gains of H₂ baked out parts, allowed to estimate the conformal film thickness T of the carbon infiltration and the hydrophobic film deposition processes.

2.3.3 Contact Angle: A small, deionized ($>17\text{ M}\Omega$) water drop was dispensed from a thin syringe needle on the top or bottom side of a c-VACNT structure. The static drop was observed with backside illumination using a digital camera. Image processing analysis was then used to extract the contact angle θ_{CB} . In many cases (especially after the surface roughing experiment 3 described in section 2.2.4 and shown in Fig. 3) the water droplet was nearly impossible to place in a stable position without having it rolling off the ct-VACNT surface before a stable image could be grabbed due to a slight tilt angle. To be able to make approximate contact angle measurements a side Teflon surface was used to localize the water droplet (trapping it locally) so that a stable image could still get be acquired. While this was not ideal and slightly influenced the contact angle measurement accuracy (lowered the highest contact angle measurements), it was determined a sufficiently accurate measurement for the intended purpose, since we were primarily interested in the contact angle decay rate, not its highest value measurement.

2.3.4 Contact angle longevity: To measure the change of the contact angle θ_{CB} over time, test samples were submerged in deionized water in a covered petri dish between two contact angle tests and weighted down with two Teflon tape encapsulated weights

(nuts) near two opposing edges to 1) minimize surface damage at the testing location and 2) to keep them continuously submerged between tests. The water in these Petri dishes was filled up when the level drops and replaced from time to time. Between tests, a Petri dish lid was placed over the open Petri dish to minimize dirt falling into the water bath with the submerged test sample. Before each sample contact angle test, the two weights got removed. Typically, the sample jumps to the top water-air interface level once one weight got removed, even if their interior surfaces remained only partially dry. Frequent handling of these test parts possibly lowers these contact angle measurements (by locally abrading the Teflon coating from the most exposed tips of the VACNTs) and/or making their data acquisition noisier. These initial experiments suggested that another test method (gas transfer rate test) would perhaps be more application relevant and provide a more realistic durability value of the hydrophobic surface modification of the nanoporous sponge structure of the ct-VACNT structures. To gain faster insights the 1st subgroup of test samples was processed with their top surface on top and 2nd subgroup of test samples with their bottom surface on top. The orientation for each subgroup was maintained during the whole longevity testing period.

2.3.5 Gas transfer *rate test*: ct-VACNT structure (made with the Experiment 3 method for the 2.2.4 surface roughening process step), like the one shown in SI Fig. 4 in the form of a Fluid channel Array Brick (FAB) were incorporated in fluid reactor test device and water was flown through the fluid channel shown in Fig. 3. O₂ gas transfer rate versus water flow rates was measured between the fluid channels and the outside of the test ct-VACNT structure. The test setup is described in section SI Fig.6. This allowed establishing a respective temporary O₂ gas transfer rate test series which is also

a representation of the dryness (and therefore hydrophobic nature) of the nanoporous sponge structure in between these inside and outside test surfaces.

2.3.6 Gas transfer rate stability test: Between two consecutive O₂ gas transfer rate test series, these test devices were submerged in water so that both the inside and outside of these ct-VACNT structures were continuously exposed to water. Before each new O₂ gas transfer rate test series, the sidewalls of the ct-VACNT structures were quickly dried with a dry sweep gas to remove any exterior water before the new O₂ gas transfer rate test series was started. Since the surfaces with this test could not get mishandled between consecutive tests, this new test method allowed a more application-relevant time dependence on the hydrophobic stability of the nanoporous sponge surface modification. It was therefore initiated after the initial contact angle testing as the experiment 3 method proved promising.

3. Results and Discussion

Native c-VACNT structures even after the H₂ treatment cleaning step are hydrophilic and have a contact angle of $\theta_{CB} \approx 70^\circ$ (see Fig. 4a). When c-VACNT structures get exposed to water all the pore volume of the nanoporous sponge material gets filled with water after some delay. That means, if they get placed on top of a water-filled Petri dish, these structures start to sink to the Petri dish bottom after some time delay (typically in *1-30 min*) and then stay there.

For applications that require that the nanoporous sponge material stays dry when parts of the c-VACNT structure get exposed to aqueous liquids (for example the top, bottom, and perforated fluid channel surfaces shown in Fig. 2) the surface energy of its nanoporous sponge material need to be modified so that both the interior and exterior

surfaces of these structures become, and ideally stay, hydrophobic for a very long time. Only when sufficient longevity of hydrophilic surface-modified c-VACNT structures has been demonstrated, related medical and/or industrial devices that incorporate such modified c-VACNT structures become commercially viable. Depending on the applications, that can require at least *1 - 12 months* of continuous liquid exposure. The purpose of this research is to find a commercially scalable way to make *> 12 month-long* hydrophobic performance possible for such modified c-VACNT structures.

Teflon is a hydrophilic ($\theta_{CB} > 90^\circ$) polymer coating that has one of the highest known contact angles for a flat surface. A flat Teflon AF 2400 film surface has a contact angle $\theta_l \approx 105^\circ$ according to its manufacturer's literature and it is generally a very inert surface that chemically does not bond easily to other surfaces¹⁷. The combination of hydrophilic films with rough (porous) surfaces is known to further increase the contact angle of such structures. The Cassie-Baxter equation (lotus leaf effect)^{18,19}, (see SI equation 1) describes the dependence of the contact angle θ_{CB} on the contact angle θ_l and the area fractions f_{SL} and f_{LV} of the solid-liquid and liquid-vapor interfaces.

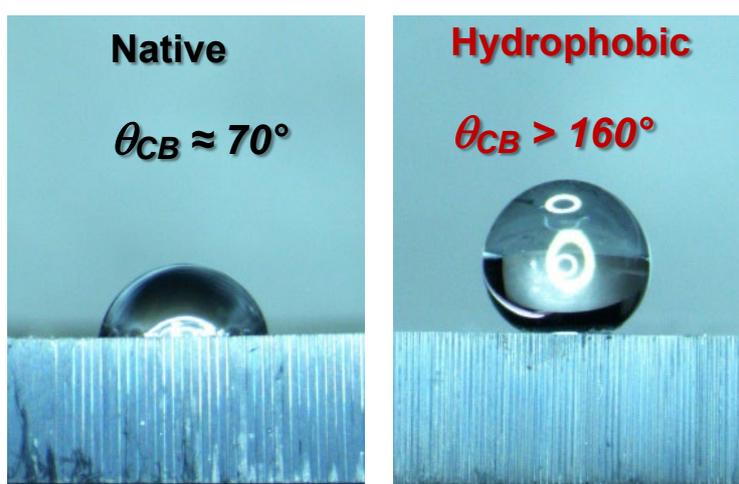


Fig. 4: Contact angle of a deionized water droplet placed on native (left) c-VACNT, and on superhydrophobic coated ct-VACNT (right) structure.

Micron tall CNT surfaces coated with a PTFE coating applied with a hot filament chemical vapor deposition (CVD) process coating process have been shown to result in a surface with a superhydrophobic contact angle $\theta_{CB} \approx 160-170$. However, this CVD process results in a non-uniform polymer deposition throughout a VACNT structure with a maximum penetration of about four times the diameter of a perforation through-hole. Therefore, for taller than $100 \mu\text{m}$ c-VACNT structures such a CVD-based PTFE coating process is not suitable to create a uniform hydrophobic surface throughout the porous material that allows it to stay dry when some part of its outer surface is exposed to aqueous liquids. In addition, for example, c-VACNT structures with a height $h \approx 2 \text{ mm}$ and with an array of $\phi \approx 50 \mu\text{m}$ diameter through-holes can only be coated to a depth of about $200 \mu\text{m}$ near its top or bottom surface. Further, the nanoporous sponge material filling the space between such through-holes remains essentially uncoated except near its top surface layer, which makes such a method unsuitable.

Therefore, to create superhydrophobic c-VACNT structures that can stay dry when in contact with aqueous liquids, we developed a novel and much lower cost PTFE coating method (see section 2.2.5) that is capable of 100% infiltrating mm tall nanoporous c-VACNT structures and that can substantially uniformly and conformally coat all surfaces of the nanoporous sponge material with a thin (a few nm thick) polymer film. Fig 4b shows the resulting contact angle of such processed ct-VACNT structure resulting in a contact angle of $\theta_{CB} > 150-170^\circ\text{C}$, depending on the prior (see section 2.2.4, experiment 3) surface roughening process steps. When such ct-VACNT structures were put in water they floated right away to the top. When they were pushed respectively to the bottom of a water-filled beaker, they jumped to the top surface as soon as they get free. If they were weighted down with a weight, they tend to slip off the weights when a slight asymmetry was present. In short, these ct-VACNT structures

remain dry after they jumped to the top surface of the water, even after being submerged for some time.

Preliminary fluid testing of ct-VACNT structures like those shown in SI Fig. 4 and Fig. 3 with fluid channels with a diameter $\phi \approx 50 \mu m$ has shown that they have a liquid entry pressure $LEP > 15 \text{ PSI}$, which was also the testing limit of the available test setup.

Initially a gas phase HMDS vapor deposition method was tested on native c-VACNT structures. Given the surface roughness of the nanocarbon sponge material, they resulted in an initial contact angle $\theta_{CB} > 120^\circ$. However, within *10 - 60 minutes* after this deposition process, the surface became hydrophilic, and the water drop got sucked into the sponge structure. To overcome this hydrophobic longevity problem, we developed the liquid Teflon deposition process described in section 2.2.5. With that hydrophobic surface modification, the resulting ct-VACNT structures stayed dry when submerged in clean (deionized) water at least overnight.

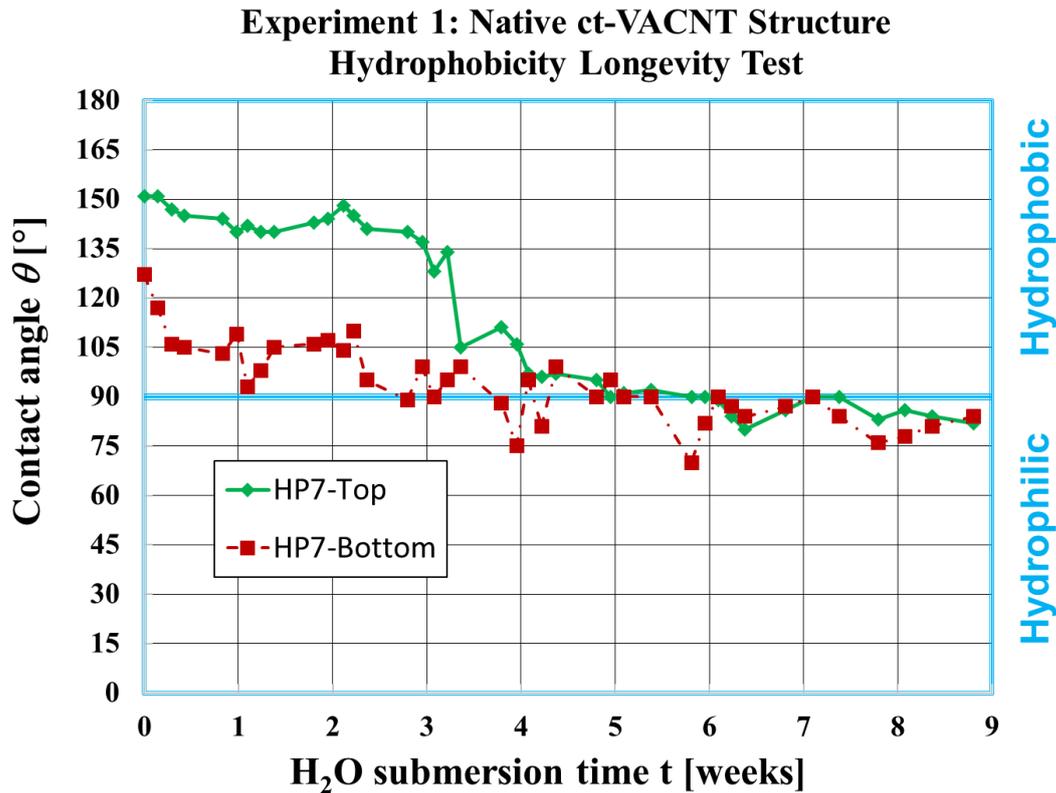


Fig. 5: Hydrophobicity longevity testing of top and bottom side of native ct-VACNT structures.

To further test the extent of the longevity of the newly developed novel hydrophilic surface modification of the native c-VACNT structures the time-dependent contact angle measurement was developed that is described in sections 2.3.3 and 2.3.4. In a first experimental series, ct-VACNT structures were built and tested without any surface modification of the native c-VACNT structures (2.2.4.1 Experiment 1) before the hydrophobic surface modification process described in section 2.2.5. Fig. 5 shows the obtained test results for a representative sample of a top and bottom surface of such processed ct-VACNT structures. Experiment 1 showed 1) the longevity of the hydrophobic coating increased from hours to multiple weeks, 2) that the bottom surface had both a lower initial contact angle than the top surface, and 3) that the bottom / top surface lasted less than 3 / 5 weeks before they became hydrophilic, i.e., before the contact angle degraded to $\theta_{CB} \approx 90^\circ$. The 2nd observation can be explained with the Cassie-Baxter equation (see SI Equation 1) since the bottom surface (see Fig. 4a) had a

significantly less surface roughness than the top surface (see Fig. 4b), i.e., the bottom surface has a lower roughness, i.e., $f_{LS} \approx 1$ and $f_{LV} \approx 0$. To explain the 3rd observation, we formulated a working hypothesis that since the thin Teflon film has practically no chemical adhesion towards the underlying nano-carbon surface it is, therefore, more easily locally removable (peelable) from the much smoother bottom side than the much rougher top side. Such local Teflon coverage loss through local peeling could be caused by liquid flows, handling during contact angle testing (for example surface drying with paper tissue before depositing new water droplet, and/or during positioning and weighting the samples back down to the bottom of the Petri dish after each contact angle test.

To further validate this working hypothesis, we decided to intentionally surface rough (abrade) the top and bottom surface of the c-VACNT structures before the hydrophobic deposition process described in section 2.2.5. Experiment 2 in section 2.2.4.2 describes the selected process roughening steps (vibratory polishing) used for the next series of contact angle longevity tests that are reported in Fig. 6. SI Fig. 5 shows the resulting modified bottom (a) and top (b) surface of such roughened c-VACNT structures compared to the native surface shown in Fig. 2a and 2b. As these images show, the bottom surface has now fully open fluid channels (no partial floor layer covering), and the smooth carbon film connecting the bottom CNT tips has been roughened by breaking it down to many small islands having an average diameter in a few μm range with cracks in between these remaining carbon film islands. The top surface has its top “crust” layer removed and has now thinner and more vertically exposed CNT tips.

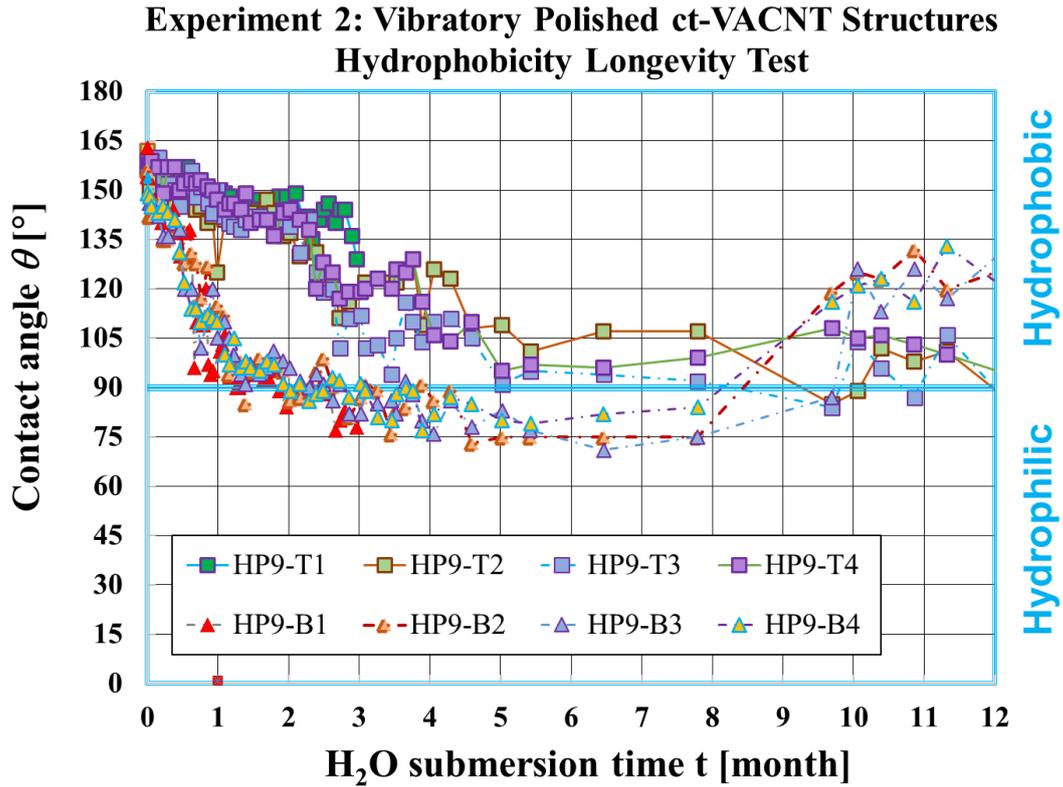


Fig. 6: Hydrophobicity longevity testing of vibratory polished top and bottom side of ct-VACNT structures.

The results shown in Fig. 6 support the above-proposed working hypothesis by 1) showing that the starting contact angle of the bottom surface is now increased and closer to the top surface due to its increased surface roughness caused by the vibratory polishing process. It further shows that the longevity of the bottom surface for Experiment 2 samples has been now extended from 2 weeks to >1.5 months but is still significantly lower than that of the top surface. Similarly, the top surface hydrophilicity has now been increased from 5 weeks to > 8-10 months.

However, we also observe in Fig. 6 that there is a very large hydrophobic longevity variation from sample to sample. We hypothesize that the large variation from sample to sample is arising from polishing impurities leftover from the polishing process (sample to sample dependent) and from the imperfect surface roughening of the bottom surface (see SI Fig. 5a) still leading to on average a faster debonding of the hydrophobic

film from the bottom surface compared to the top surface and/or process stability imperfections. The remaining embedded polishing material in the near polished surfaces region, which is much larger than the nano-sized CNTs, can over time pull out and remove any local hydrophobic PTFE film coating, thereby degrading the local contact angle. Therefore, the conclusion from Experiment 2 is that hydrophobic longevity of > 12 months is possible, but the vibratory polishing process needs to be replaced with a more consistent and residual free surface roughing process, and ideally also with one that is more volume scalable.

To validate this expanded working hypothesis, we tested another surface roughing process to modify the bottom and top surface of the c-VACNT structures before the hydrophobic deposition process described in section 2.2.5. Experiment 3 in section 2.2.4.3 describes a chosen low-pressure O₂ plasma process to selectively burn the top and bottom surface to surface roughing it, which we used for the next series of contact angle longevity tests, reported in Fig. 7. SI Fig. 3 shows the resulting modified bottom (a) and top (b) surface of such roughened c-VACNT structures. The O₂ plasma process roughens the surface by burning edges faster than the more thermally connected surfaces between them. This leads in addition to the transformation of the substantial 2-dimensional starting surface (Fig. 2) to a more 3D-dimensional final surface (Fig.3). Fig. 2 and 3 show that the edges of the fluid channels near the external surfaces burn the fastest (sharpest corners) therefore leading to a rectangular to round funnel conversion into the inner fluid channel cylinders. The depth of these funnels depends on the O₂ plasma process recipe and c-VACNT surface side. For each surface side, it primarily depends on the O₂ plasma on-time, plasma power, substrate preheat temperature, and O₂ concentration of the plasma gas. Due to the difference in the top surface “crust” layer, the bottom side requires $\approx 20X$ less plasma on time for otherwise

similar plasma recipe conditions to obtain a similar 3-D funnel structure and surface layer removal depth for the top and bottom surface.

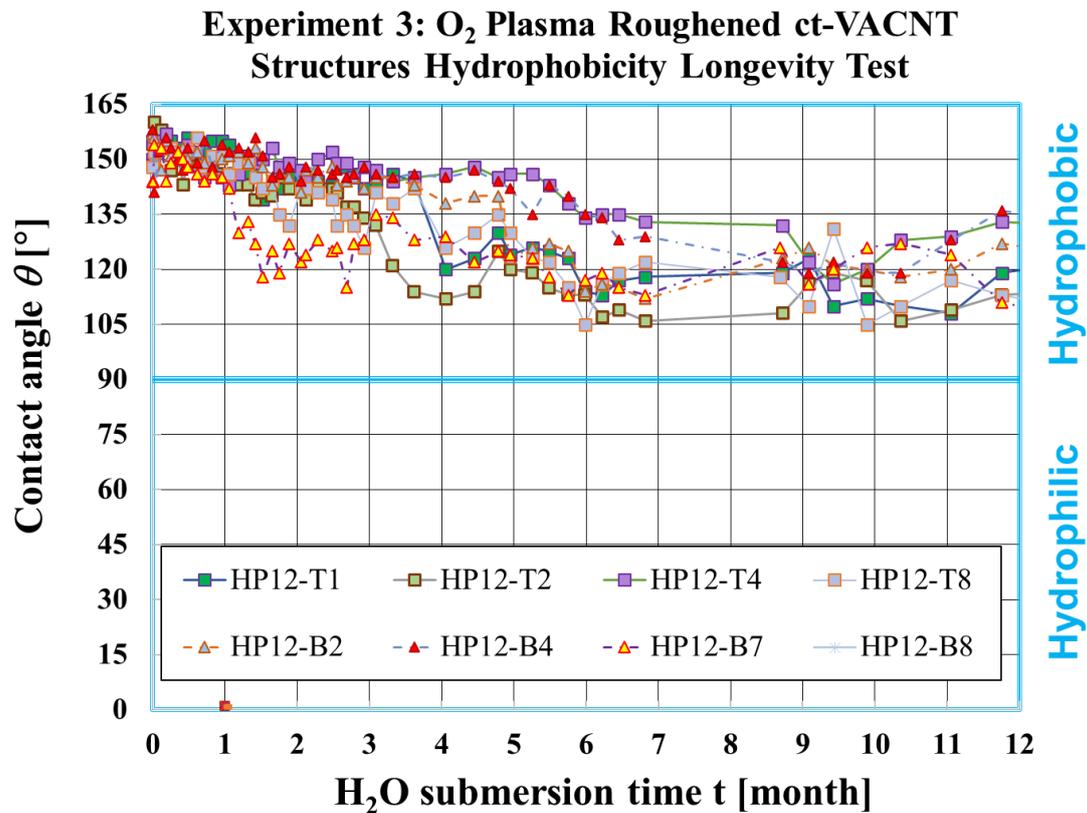


Fig. 7: Hydrophobicity longevity testing of O₂ plasma top and bottom surface roughened ct-VACNT structures.

Fig. 7 shows the time dependence contact angle change for ct-VACNT samples prepared with Experiment 3 (see section 2.2.4.3) surface roughening method. This time the bottom and top surface have a much more similar contact angle starting value and similar longevity time dependency that exceeds 12 months. Fig. 7, therefore, validates our hypothesis that appropriate surface roughening of the top and bottom c-VACNT structures before applying the hydrophobic coating is the key to dramatically increase its longevity.

There is a possibility that the chosen contact angle measurement technique and its in-between measurement chosen water submersion technique contribute to the slow

contact angle degradation over time. Therefore, we developed another technique to measure the longevity of the hydrophobic coating of the c-VACNT structure by measuring the gas transfer rate stability between the fluid channel and the exterior sidewalls of ct-VACNT structures, similar to the one shown in SI Fig. 4. Specifically, we used rectangular type samples with a length of 30 mm and a width of 5 mm and with fluid channel diameters $\phi \approx 45 \mu\text{m}$ and $65 \mu\text{m}$ spacing on a rectangular grid. We further used deionized water as fluid media and measured the O_2 gas transfer rate over time.

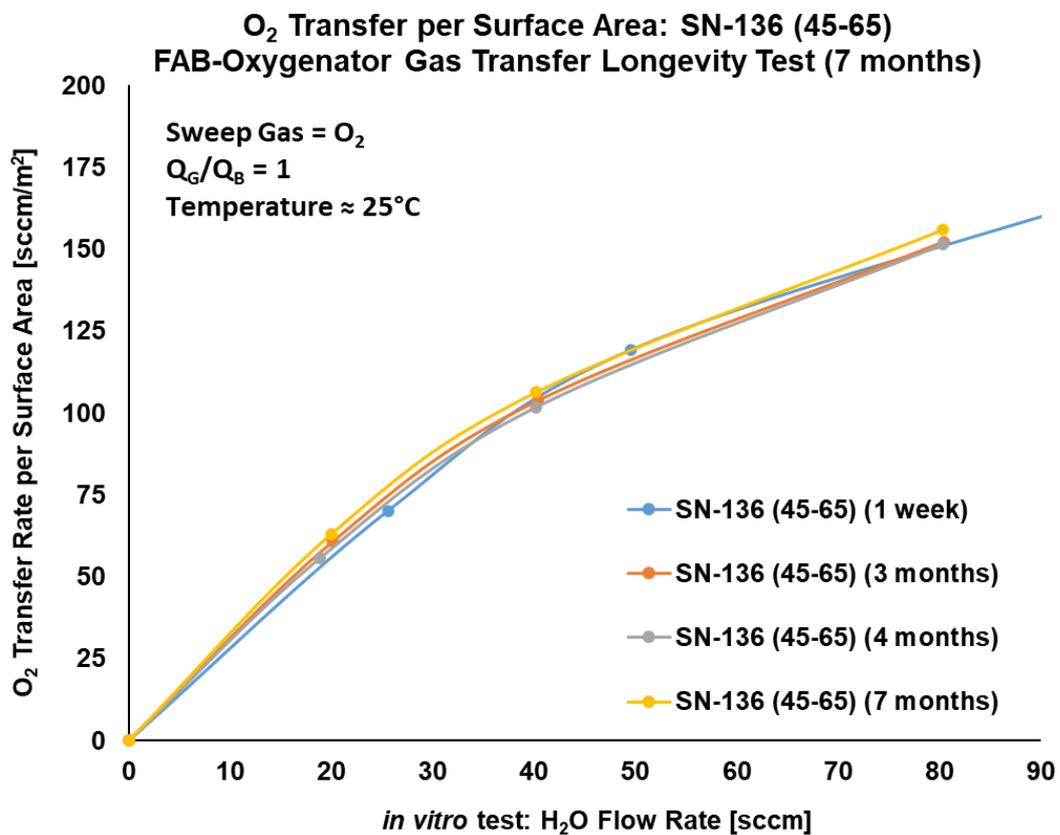


Fig. 7: Hydrophobicity longevity testing of O_2 plasma top and bottom surface roughened ct-VACNT structure in the form of a FAB inside a test FAB-Oxygenator

This even more application relevant non-contact measurement shows the longevity of the gas transfer rate through the nanoporous structure of the ct-VACNTs in the form of a FAB inside a custom FAB-fluid reactor test device that exposes the ct-VACNT

structure of such a FAB to water on all sides between gas transfer tests, as discussed in section 2.3.6. Fig. 7 shows that there was no significant change in the gas transfer rate over a 7-month measurement period, indicating that the interior of the nanoporous ct-VACNT structure stayed dry for all this time and showed much better stability than shown in Fig. 6.

4. Conclusion

Native c- VACNT structures are slightly hydrophilic and therefore need to be modified for applications that require hydrophobic behavior. We accomplish this by conformally overcoating the nanoporous sponge structure of which all c-VACNT structures are made off with a few nm thick hydrophobic Teflon-like film, thus creating a ct-VACNT structure. Such a conformal film was demonstrated for up to a few mm tall c-VACNT structures using a key liquid Teflon deposition process that allowed Teflon dissolved in a suitable solvent to uniformly penetrate the nanoporous 3D sponge-like material, thus filling all the respective void space with dissolved Teflon at the same concentration. A subsequent slow drying process allowed the local available Teflon material to deposit uniformly to the nearest surfaces, thereby substantially uniformly coating all the surfaces of the solid structure of the nanoporous material with a thin film that, while not chemically bonded, was held in place (just like a sleeve over bend arm) by the kinks and twists the VACNTs and was further anchored by their frequent carbon spot welds that made it nearly impossible to slide the hydrophobic polymer sleeve from the nanoporous structure, unless the whole nanocarbon sponge structure was locally damaged. Initial contact angle tests over time showed that the longevity of the bottom surface was significantly lower than that of the top surface, which was attributed to the additional carbon film that covered the CNT endings at the bottom of the structure,

which was smooth and provided locally nearly no mechanical feature to hold the polymer film in place.

To increase the longevity of this hydrophobic coating several surface roughening methods before the hydrophobic polymer film application were evaluated together with contact angle longevity tests for both the top and bottom surface. In conclusion, an O₂ plasma process proved thus far as the best surface roughening method extending the longevity of both the top and bottom surface of ct-VACNT structures to over one year. This method also provided the most consistency, uniformity, and volume manufacturing scalability surface roughness modification method and is additionally tunable to various ct-VACNT structure application needs. In addition, a gas transfer longevity (stability) test was performed for over 7 months for ct-VACNT structures in the application-specific format of a fluid channel array brick (FAB) with distilled water as fluid and O₂ as transfer gas from outside such a FAB, through its nanoporous nanocarbon sponge material into the internally located array of fluid channels filled with flowing water. Even better than the contact angle longevity test, this gas transfer test showed that the hydrophobic sponge forming such a FAB stayed dry over the 7-month test period and therefore confirming that over this 7-month test period the hydrophobic coating stayed in place and did not deteriorate measurably.

Therefore, these longevity tests showed that such created ct-VACNT structures, in particular when surface roughened with O₂ plasma before a conformal deposition of a thin film of a hydrophobic material over all surfaces of their nanoporous sponge material, are sufficiently stable to warrant consideration for various medical and industrial application that use aqueous liquids and require a long life gas transfer stability in and/or out of an incoming liquid to achieve a targeted output liquid modification.

Supporting Information

Additional supporting information can be found in the Supporting Information document.

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