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Wetting of Nanotubes

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Abstract:

Wettability studies of liquids inside nanometre scale channels commenced shortly after the discovery of carbon nanotubes in the early 1990s. Since then the field has progressively expanded to other kinds of nanotubes and nanochannels as they have become available. This paper offers a critical review of wettability studies inside and outside nanotubes and nanochannels published in the last three years (2008-2010). The review focuses in particular on three areas, the wetting behaviour of water and aqueous fluids inside nanotubes, the wetting of polymers inside and outside nanotubes and the wetting of nanotube arrays or forests. The authors believe that there is scope for further growth of this research area as there are a number of interesting topics that deserve further investigation.

1 Introduction

Wettability studies of liquids inside nanometre scale channels commenced shortly after the discovery of carbon nanotubes in the early 1990s [1, 2]. The field has progressively expanded to other kinds of nanotubes and nanochannels as they have become available. This paper offers a critical review of wettability studies carried out inside and outside nanotubes and nanochannels published in the last three years (2008-2010). Readers interested in reviews on the topic for previous years are directed elsewhere [3, 4].

The 2008-2010 period has not seen major advancements in theory, and in particular on whether – and how – nanometre scale confinement affects wetting. On the other hand, there has been a substantial increase in the number of publications on experimental results, a major change from the past when most papers where based on numerical simulations [3, 4]. The topic of wetting at the nanometre scale cannot be investigated without looking at studies of the flow of liquids inside nanochannels, as the channel wettability plays an integral role in the flow of liquids through it [5]. A coherent theoretical framework relating wettability to fluid flow in nanochannels is still missing despite a large number of experimental papers having been published, and this represents one of the most promising areas of investigation for interested researchers. Whereas in the past this topic has captivated scientists' attention due to unusual behaviour, like higher than expected flow rate through carbon nanotubes, recent publications have started focusing on the applicability of nanoscale flow, in particular for filtration and water desalination.

Another area of intense research has been the wettability of nanotube arrays or forests mostly to obtain superhydrophobic surfaces or tunable ones. There is abundant literature on both topics and the increased possibilities of fine tuning offered by advanced nanotube arrays methods have vastly expanded the range of materials prepared.

This review will attempt to select the most notable results on wetting of liquids inside nanotubes and nanochannels as well as wetting on nanotube arrays and present them in a coherent and critical vision. The review will conclude by focusing on the most interesting challenges from both the scientific and applications points of view for the next few years.

2 Theoretical Aspects

The fundamental equations regarding wetting are well established and will not be re-analyzed here. Interested readers are directed to a comprehensive text on the topic [6]. The effect of nanoscale confinement on wetting, though, is still a matter of intense debate and will be briefly reviewed here. For the case of a liquid drop on a flat substrate, a classical modification to Young's equation has been proposed:

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} - \tau\kappa \qquad (1)$$

where θ is the contact angle, γ is the surface tension with the subscripts for Liquid, Vapour, and Solid, respectively, τ is the line tension of the triple line and κ is the curvature of the triple line. Atomic force microscopy (AFM) and modelling have shown the validity of this equation for nanometre size drops with a circular triple line ($\kappa \equiv R$) of radius R [7]. In particular, theoretical results are based on modelling a

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liquid drop on a substrate (with $\theta > 0$) as an inextensible membrane subject to stresses (the surface tension) varying along the surface of the drop and at the interface with the liquid. The major outcome of this work has been to provide a coherent derivation of the line tension τ - having a positive value - as a function of the interactions between the liquid and substrate. The model also includes the effect of surface roughness and/or anisotropy on the contact angle in the line tension term rather than using empirical parameters as in the Wenzel or Cassie-Baxter models. This model though, does not consider the potential effect of nanometre scale confinement on the surface tension itself, as has been postulated by many papers (cfr [6]), nor makes explicit the nature of the molecular interactions between the liquid and the solid in terms of surface tension components, perhaps using well known models from Fowkes, Good, Zisman, Van Oss and, more recently, Li and Neumann [6, 8].

The picture gets more complex when considering wetting inside nanochannels or small capillaries. The basic equations for capillary filling are well known and the Washburn equation connects the filling process with the wetting (or not) of capillary walls by the liquid. If one considers a channel with a circular cross-section, as the Washburn equation does, then the line tension will no longer be parallel to the substrate as in the flat case, but perpendicular (Figure 1).
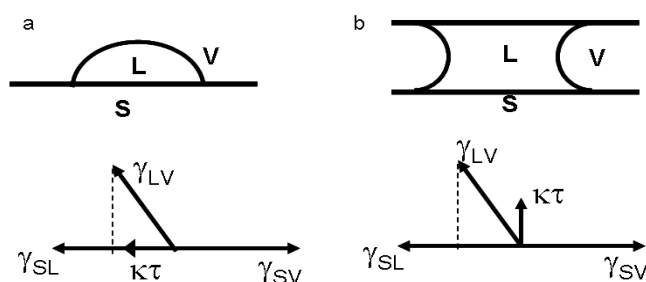

Figure 1. a) Schematic of a liquid partially wetting a substrate and surface tensions vector summation at the triple line. b) Schematic of a liquid plug in a channel with circular cross-section and surface tensions vector summation at the triple line.

The effect of the line tension in nanochannels is difficult to assess. A recent publication showed that the apparent diameter of large carbon nanotubes (~200 nm in diameter) decreases upon filling with water [9]. In reality, the tubes only recovered their minimal energy shape (having a circular cross-section), whereas they tended to flatten due to van der Waals attraction and weak mechanical properties when empty. The recovery of the minimal energy shape in the tube can be attributed to the radial component of γ_{LV} acting on the liquid plug when the tube gets filled. At this stage it is not possible to determine whether the line tension, in this case acting along the radius of the tube (Figure 1b), has played any significant effect. Given the tubes large diameter and small value of the line tension one can only imagine that the effect was negligible. With smaller tubes, though, this might no longer be the case. Similarly, flow in nanometre channels induced solely by surface tension asymmetries between immiscible liquid drops has been shown in MD simulations [10].

An important aspect to consider is the presence of a monolayer of liquid adsorbed on the capillary walls preceding the advancing meniscus. Molecular dynamics (MD) simulations have shown that the presence of such precursor films in capillary filling of nanometre channels leads to the deformation of the meniscus profile from the ideal

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circular cross-section [11]. This distortion can be attributed to the interaction with the boundary surface (the wall) and the disjoining pressure induced by molecular interactions between the fluid and the solid (Figure 2).
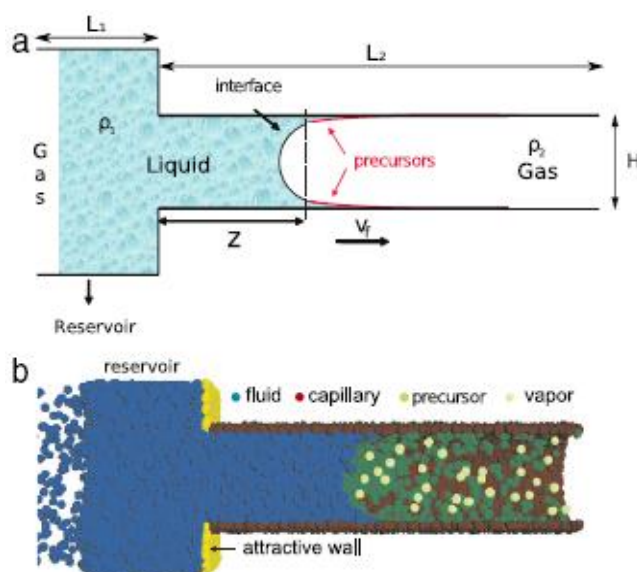

Figure 2. a) Schematic of the geometry used to simulate capillary imbibition of a wetting fluid in smooth and rough capillaries; b) Snapshot of MD simulation showing fluid imbibition and the formation of thin precursor films ahead of the capillary front [11].

As the thickness of these precursor layers or any other thin film approaches the nanometre scale, the effect of long-range forces (van der Waals, double layer forces) becomes significant. Their effect on macroscopic wetting is well known and can be described using the disjoining pressure [12]. Recently, the effect on wetting of nanometre scale films of the presence of nanoparticle dispersions has been investigated, showing that for film thicknesses comparable with the nanoparticle size, the latter tend to assume an ordered structure, reducing film pressure and, thereby, increasing the spreading of the liquid [13]. When considering the advancing meniscus in a nanotube or nanochannel, the thickness of the wetting (or precursor) film in front of the meniscus can be comparable to the channel characteristic size (radius or height) [12]. In the partial wetting case, the contact angle can be calculated by extending the curvature of the central part of the meniscus, where the disjoining pressure does not act, to the surface of the solid. When there is complete wetting of the film, the radius of the meniscus can be calculated by equating the capillary pressure generated by the meniscus curvature to the disjoining pressure of the film, as first detailed by Derjaguin [14]. It should be noted that TEM micrographs of water plugs inside 2-4 nm diameter carbon nanotubes have shown that the liquid does not form a continuous, well defined meniscus [3], while precursor films have been experimentally observed only for larger tubes (>100 nm diameter) so far [9]. In addition, there are conflicting modelling results on the validity of the continuum assumption down to such small scales [3], casting some doubts on the validity of using concepts such as menisci and precursor films at these small scales , as described above.

Surface roughness also has a significant influence on wetting under nanometre scale confinement. The well known Wenzel and Cassie-Baxter equations explain the macroscopic wetting on patterned and rough surfaces, respectively. A recent paper

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looks at whether the Wenzel equation can be used at the nanometre scale, and found that it no longer works when the periodicity of the surface patterns is less than 10 nm [15]. Interestingly, this is in the same range where a breakdown of the continuum model has been postulated after higher than expected flows in carbon nanotubes have been observed [3].

The concept of roughness inside nanochannels is quite different from the macroscopic case since the characteristic size of the roughness is comparable to the channel size. As such, experimental observations of the effect of roughness on wetting of liquids inside nanotube or nanochannels have not yet been published, to the authors' knowledge. On the other hand, a substantial number of results on this topic have been published using molecular dynamics simulations.

An interesting simulation looked at the effect of hydrophilic and hydrophobic rough channel walls on liquid flow and found that flow rate was higher for rough hydrophilic than smooth hydrophobic surfaces [11]. This result runs contrary to general belief that hydrophilicity and roughness both reduce the flow velocity by increasing drag [16]. The higher flow velocity has been attributed to the presence of a precursor film on the channel wall that would shield the wetting fluid from the rough surface. It is necessary to note here that the authors consider 'hydrophobic' to be a surface wet by a liquid forming a contact angle of 30 to 40˚. MD simulations of flow through nanotubes and nanochannels typically use much higher values of contact angle for hydrophobic surfaces [17]. In addition, the roughness was simulated by adding a single rectangular obstacle inside the channel whose height can be varied to observe the effect of roughness on the meniscus.

A broader study compared the effect of different surface chemistry and roughness on water flow (and thus wettability) in a CNT, a boron nitride nanotube (BNNT), a silicon nanotube and in a roughened nanotube [17]. The simulations found that there was a plug-like velocity flow profile with a 'jump' in velocity at the solid-fluid interface (Figure 3). This was observed with all the nanotubes except the rough structured nanotube and the largest enhancement was observed within the (16, 16) CNT, for which a hydrophobic structure is assumed. This is a somewhat debatable assumption and the choice of specific values for the Lennard-Jones interaction potentials can dramatically alter the result of MD simulations [3]. The velocity 'jump' has been attributed to nano-bubbles forming on hydrophobic surfaces, resulting in ballistic flow profiles [18]. The authors imposed hydrophilic Lennard-Jones parameters on the structure of the CNT to simulate the effect of a low contact angle condition (Figure 3 iii). The simulation still showed a plug-like velocity profile in this case as well, albeit at much lower level. This is somewhat surprising since one would expect that in the wetting case the velocity profile should be closer to the parabolic type with zero velocity at the wall, since the liquid wets the surface. It should also be noted that whereas for all three simulations with smooth walls, the water concentration peak is situated at a distance from the wall that reflects the size of the water molecule, this is not the case for the rough channel. This difference can be attributed to the irregularity of the surface and could potentially be modelled effectively using the Cassie-Baxter equation.
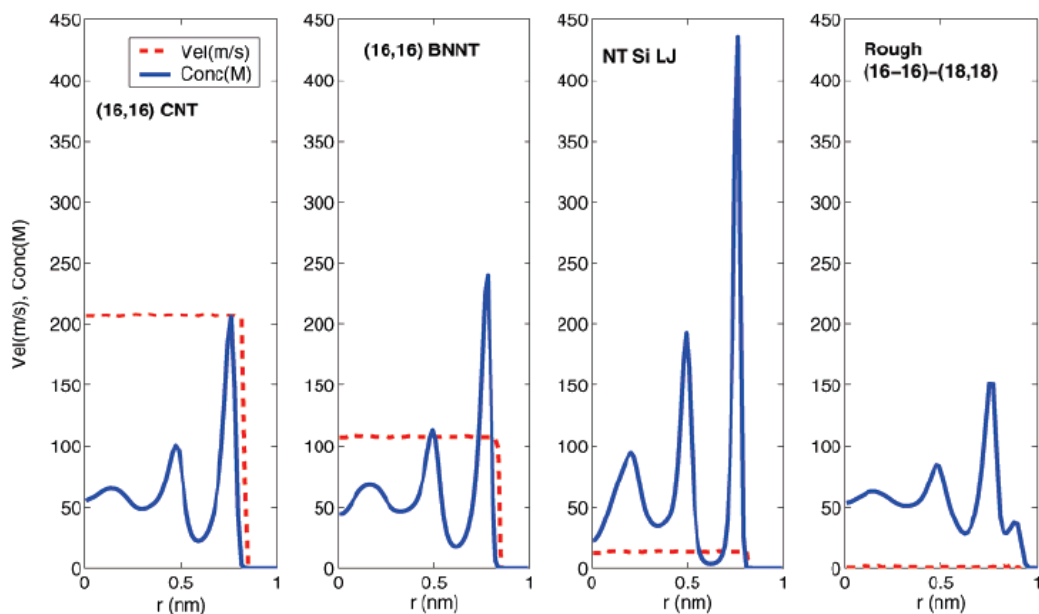
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Figure 3. 'Water concentration and axial velocity profiles as a function of the radial distance toward the wall from the centre of the tube at r = 0 nm. Only one-half of each tube cross-section is shown. From the left to the right are (i) (16, 16) CNT, (ii) (16, 16) BNNT, (iii) (16, 16) NT with Si LJ (iv) rough tube with alternating sections of (16,16) and (18, 18) tubes. For the first three cases, even though the tubes have smooth surfaces, the magnitude of the flow velocities show marked differences. The bulk concentration is 55 M'. [17]

As discussed in the introduction, several open questions remain regarding if and how wetting is affected by nanometre scale confinement. Despite these limitations, a large wealth of experimental evidence on the topic is accumulating and will, probably, lead in a short time to breakthrough discoveries on the theoretical front as well.

3   Wetting of Nanotubes by Water and Aqueous Fluids

Earlier reports showing that water and other liquids had unexpectedly high flow rates through sub-10 nm diameter carbon nanotube membranes has led researchers to investigate their use as filters for water desalination [3]. Molecular dynamics simulations of reverse osmosis of a potassium chloride solution through a nanotube has shown a 10-fold increase in flow rate for carbon and boron nitride nanotubes compared to currently used polymeric membranes for the same applied pressure [19].

Ion exclusion experiments in sub-2nm diameter CNT membranes have indeed shown superior water fluxes compared to commercial polymeric membranes [20]. The wettability of the tubes (from hydrophobic, due to synthesis conditions, to hydrophilic) has also been altered by bonding carboxylic groups to the tube ends, to enhance ion selectivity [21].

As discussed earlier, the wall surface chemistry and structure can have substantial effects on the wetting and, hence, the flow of liquids inside nanotubes (Figure 3). Experiments in larger diameter CNTs (~40 nm internal diameter) have shown substantially smaller increases in fluids flow for different liquids [22, 23]. These can be attributed not only to the larger size, but also to the different surface chemistry and structure of the tubes used. Unlike smaller tubes, these have been produced by non-catalytic CVD, yielding a turbostratic (or amorphous) graphitic structure whose

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wettability can be easily altered to become hydrophilic [3]. The effect of the tube diameter on the flow rate enhancement was also investigated via MD, showing that it decreases with increasing CNT diameter [24]. The presence of defects on the surface of nanotubes can also significantly slow down fluid flow inside CNTs by altering the nanotube wettability [21]. Although a direct correlation between the presence on the nanotubes' surface of defects and liquid flow rates through them has not been established, there are several results in the literature showing that the former reduces the contact angle of liquids inside carbon nanotubes, making them hydrophilic [3]. In turn, simulations have pointed to the fact that higher than expected liquid flow rates should occur only in hydrophobic tubes. This theory has not yet been verified experimentally.

Simulations also suggested that inside small CNTs (1.66nm internal diameter) the effective water viscosity is smaller due to the increased ratio of interface to bulk volume [25]. By calculating the variation of water viscosity and slip length as a function of CNT diameter, it has been found that the results can be fully explained in the context of continuum fluid mechanics. A distinction between interfacial and bulk liquids is common in MD simulations of fluid behaviour inside nanotubes (Figure 3). It should be noted, though, that sometimes it appears questionable: In a 1.66 nm diameter nanotube there are less than 6 water molecules (water molecule diameter ~0.28 nm) along the diameter. If one further considers the van der Waals radius of the water molecules (as in Figure 3), the number of liquid molecules along the tube diameter further reduces.

Wetting and flow of liquids inside boron nitride nanotubes has also been the subject of several MD papers, in general comparing their properties with CNTs (Figure 3). Simulations have been carried out for both (5,5) BNNTs and (6,6) BNNTs and subsequently compared with CNT simulation results [26]. The results implied that water molecules inside an uncharged (5,5) BNNT align in single-file within the tube. A similar arrangement of the water molecules is observed when the tube is partially charged, whilst making the tube more hydrophilic and slowing down water diffusion due to the interaction of the water molecules and the nitrogen atoms of the BNNT. Reverse osmosis experiments in (5,5) BNNT tubes have shown higher slat rejection than CNTs owing to the different wetting behaviour [27].

The experimental reports showing high liquid flow rates through nanotubes have also spurred a series of simulations papers on 'nano-pumping', using the mechanical or electrical properties of carbon nanotubes to advance liquids through them. A first paper has looked at CNTs conveying viscous fluids, with simulations showing that as the flow velocity increases, the resonant frequency for the tube's first mode vibration decreases[28]. This resulted in the activation of an axial fluid flow inside a carbon nanotube by producing Rayleigh travelling waves on the nanotube surface [29]. The driving force for such an effect would be the friction between the fluid particles and the nanotube walls. While the authors did not specify the wetting behaviour of the fluid in the CNT, they attributed the pumping effect to the presence of friction between the fluid molecules and the wall, contrary to the quasi-frictionless flow in graphitic CNTs generally considered to be occurring for water [3]. While a popular MD paper showed that flow through CNTs could be generated using localized charge effects on the CNT wall [30], its results have been recently disputed due to an erroneous use of the MD code [31], in particular regarding the interaction potentials between the liquid and CNT wall molecules. This example points to the fact that the choice of interaction potential between the liquid and tube wall molecules is

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fundamental to obtain viable results. Earlier publications have looked at this issue extensively as well as the validity of the assumption present in most simulations that carbon nanotubes are highly hydrophobic materials [3]. A recent MD study has looked specifically at liquid-wall interactions dominated by dispersive forces rather than electrostatic ones for non-polar fluids [32], mimicking the approach taken for surface tension components. Such an approach can be extremely useful for nanotubes and channels, especially for well designed systems where the values of the interaction potentials are well known, such as water-CNT.

The relation between interaction potentials and wetting has also been observed in MD simulations of the microscopic wetting of water on amorphous silica surfaces with different degrees of surface hydroxylation or silanization [33]. The contact angle in the completely hydroxylated silica surface is approximately 22–35º. On the amorphous silica surface, the contact angle of water can vary substantially, partially depending on the silanol concentration on the surface. The wetting of these surfaces can, in principle, be tailored with a monotonic increase of the contact angle for water 30º to 110º when the silanization percentage increases from 0% to 70%. Similar results have been obtained for carbon nanotubes [3].

A newly developed optical-based technique allows measurement of flow velocity profiles in nanochannels in the 50-100 nm range [34]. This is already a remarkable result and if, the resolution can be pushed below 10 nm it would allow direct observation of many of the phenomena discussed above, without the complications of operating in a vacuum in an electron microscope.

4   Wetting of Nanotubes by Polymers

The high viscosity, along with melting or glass transition temperatures above room temperature, of polymers adds a further complication to direct observation of their wetting behaviour in nanotubes and channels. To overcome these limitations, ex-post observation of the solidified, cross-linked or cooled-down drop has been used to infer information on the wetting process. In a notable example, nanometre sized droplets of polyvinylidene fluoride (PVDF), were generated using a microfluidic system and placed onto individual carbon nanotubes [35]. SEM observation of PVDF-coated CNTs after a thermal treatment showed both clam-shell and barrel type droplets formed on the outer shell of CNTs. Pure PVDF drops had an estimated contact angle above 60°, whereas the addition of ppm quantities of maleic acid anhydride (MAH), lowered the contact angle to ~20°, substantially improving the adhesion of the polymer to the CNT, a fundamental prerequisite for effective load transfer from the matrix to the fibre in polymer-CNT composite materials.

A similar approach was followed to encapsulate polymer melts inside carbon nanotubes with the objective of using the polymer as a cap for lower molecular weight liquids (chiefly water) already inside the CNT [36]. The method has been tested also for surfactants, nanoparticles in solution and low molecular weight fluids within nanotubes and microchannels. The method is based on wet intercalation of polycaprolactone (PCL) inside CNTs filled with an insoluble liquid. In one experiment, the CNTs were filled with water and immersed in a solution of PCL in toluene. The PCL molecules are led by self-sustained diffusion to the CNT open ends, but PCL cannot easily enter into CNT cavities that are filled with water, which is immiscible with toluene and a non-solvent for PCL. As a consequence, when the molecules of PCL encounter water in CNTs, they accumulate and sometimes cap the tube entrances (Figure 4).
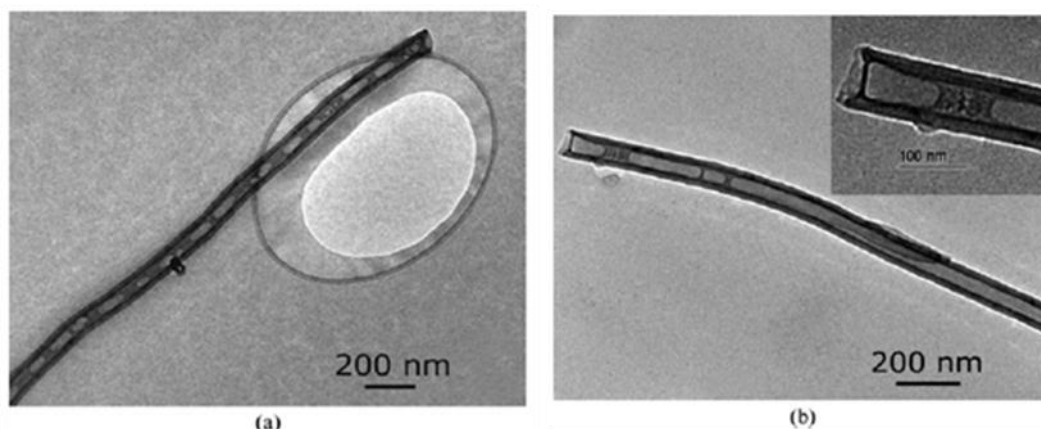
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Figure 4. Catalytically produced CNTs containing intercalated PCL (80 kDa) from a 1 wt% toluene solution. Image (a) corresponds to an initially dry CNT, while (b) shows PCL plugs at the ends of a CNT partially filled with water [36].

Wetting studies of molten PCL inside anodic aluminium oxide (AAO) templates have been performed to obtain PCL nanotubes and wires [37]. It was found that with increasing vibration frequency (from 2.0 to 14.0 kHz) the flow rate of the melt increased, which suggested that the velocity profile of the polymer melt changed from parabolic to a plug flow-like one, and with the dynamic contact angle of the liquid deviating from the equilibrium value. This effect was attributed to two factors, a first one related to the reduction in viscosity of the melt due to the disentanglement of the polymer chains; a second was due to an increase in slip length due to the applied vibrations. While the latter case appears to be a reasonable assumption, the former is probably the dominant mechanism. In fact, the use of external vibrational forces to deform carbon nanotubes to pump fluids through them has been recalled earlier [38], attributing this to friction effects between the fluid molecules and the tube walls. In the case of AAO the pore walls are rigid and further apart, but the authors have suggested that this mechanism will apply to larger space/time scales as well. Wetting experiments in polyurethane acrylate (PUA) rectangular nano channels (with width ranging from 50 to 800 nm and constant height of 200 nm) showed negative capillary pressure [39]. Several surface chemistry treatments were performed to alter the wettability of the channels. In the case of complete wetting, the formation of a precursor film in front of the meniscus was observed as well as the meniscus having convex curvature (Figure 2). For a partial wetting case, a complex meniscus shape was observed, similar to what has been observed in silicon oxide nanochannels [22]. Interestingly, for the smallest channel investigated, this complex meniscus led to a plug flow-like meniscus shape due to an overlap between the convex curvatures at the channel walls.

A molecular dynamic study investigated the wettability of nanotubes lined with polymer brushes on their inner surface [40]. The fluid was modelled as molecules interacting through Lennard-Jones potential and it was found, as expected, that the wettability of the coated tube was solely a function of the wettability of the polymer brushes, and that the imbibition rate increased with increasing length of the brush chains. During fluid uptake, the polymer brushes reorganize into alternating layers of changing monomer density due to the motion of the meniscus. A dense plug of monomer forms at the rear of the meniscus, while the polymer chains still untouched

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by the fluid exhibit little stretching and lie closer to the capillary wall. Simulations for a non-wetting tube showed that for short chain length there was no meniscus movement, while for long polymer chains no curvature of the meniscus could be identified, with behaviour consistent with that of a column of fluid rising through a porous medium.

Nanotubes of different natures have also been extensively used to modify the wettability of polymer melts and solutions. An interesting example is given by the use of halloysite nanotubes (HNTs), a kind of natural hydrophilic nanoclay, to modify the wettability of polypropylene (PP) films [41]. The HNTs act as heterogeneous nuclei for PP leading to phase separation during drying of the composites leading to the formation of hybrid micro-spherulites dotted with nanostructures. This 2-scale roughness produces a superhydrophobic behaviour with a maximum water contact angle of ~170º and sliding angle of about 2º (Figure 5).
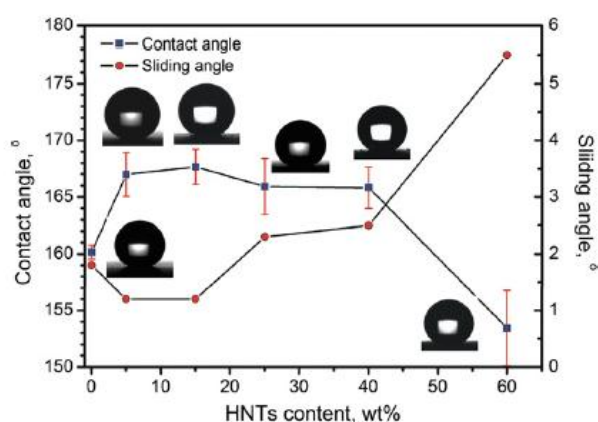

Figure 5. Contact angles and sliding angles of the PP and PP/HNTs composite surfaces[41].

Superhydrophobic films have also been prepared by solution casting of CNTs and sodium stearate (SST) [42]. Contact angle values vary linearly with the SST:CNT ratio from 150º for 0.25:1 ratio to 163º for1:1 ratio and then down to 135º for 2:1 ratio. CNTs have been used to increase the hydrophobicity of nylon-6 films, with a doubling of the contact angle value up to 101˚ for 2.0 wt% CNT loading [43]. On the other hand, carbon nanotubes have been used to increase the wettability by PMMA of larger carbon fibres by increasing the roughness of the surface [44]. Whereas simple oxidation of the carbon fibres yielded only a marginal decrease of PMMA contact angle, a 30% decrease in the contact angle was measured in the presence of the CNTs on the fibre surface. Polymers can also be used to modify the wetting behaviour of nanotubes, with particular effort placed in increasing their dispersability in aqueous media. An example is the addition of anti-foaming agents to CNT dispersions prepared via ultrasonication [45]. The anti-foaming agents eliminate air layers trapped at CNT surfaces that shield the tubes from the ultrasonic wave, increasing dispersed amounts by up to 20 times.

A promising approach to modifying the wetting behaviour of CNT-based films is by applying electromagnetic fields across the films. This method is simpler than electrowetting in terms of preparation and requires substantially lower applied voltages. The applied field modifies the electrical double layer on the CNT film surface, thereby modifying the contact angle. Wetting experiments with water and ethylene glycol have shown contact angle variations of up to 60% for a relatively low

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applied voltage of 14 V [46]. Further treatment with ammonia increased the contact angle change due to the build up of charges on the CNT surfaces.

5   Wetting of Liquids on Nanotube Arrays and Forests

The ability of geckos to walk on walls and ceilings without falling has inspired the development of several nanotubular structures to mimic the stickiness of the hairy structure of the gecko's feet. A first example is given by hard poly(dimethylsiloxane) (PDMS) nanostructures with controllable lengths, produced using AAO templates[47]. The resulting hairy structures coated on a hydrophilic substrate have shown water contact angles up to 150º, as well as high contact angles for other liquids such as glycerol (157˚), ethylene glycol (135º), dimethyl sulfoxide (97º), nitromethane (105º), propylene carbonate (135º) and olive oil (60º). These structures also have high adhesion due to the capillary rise between the pillars, with liquid droplets remaining attached to the substrate at tilt angles close to 180˚ (Figure 6a and 6b).

At the opposite end of the spectrum are titanate nanotubes arrays prepared by electrophoretic deposition (EPD) with contact angles close to 0˚ with fast spreading kinetics (Figure 6c) [48]. The arrays convert to superhydrophobic behaviour (152º) and strong adhesion after modification with a fluorosilane (Figure 6d).
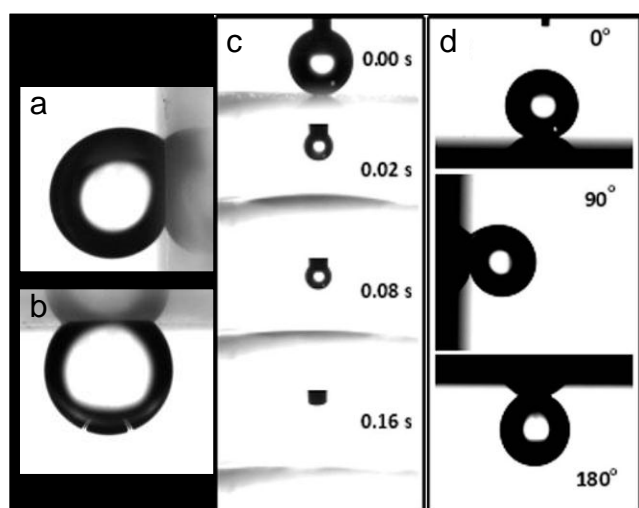

Figure 6. Water droplets on the hairy PDMS nanostructures with a) 90º and b) 180º tilt[47]. c) Complete wetting and fast spreading kinetics on titanate nanotubes; d) superhydrophobicity with high adhesion after fluorosilane modification [48].

The wetting behaviour of such nanostructured surfaces is well explained using the Cassie-Baxter and Wenzel models for wetting of structured surfaces [6]. An interesting paper has looked at the transition between these two regimes on nanopillar-like surfaces with varying pillar diameters, heights and pitch values[49]. In particular, the authors found that as the pitch increased in the 100 μm range, the static contact angle increased gradually up to 170°. While diameter and height can be easily controlled in nanotube array structures, pitch is difficult to control. In arrays based on anodization techniques, such as TiO_2, the inter-tube distance is limited by the oxide growth mechanism and is related to the voltage in the anodization process. Varying

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the density of CNT arrays is also difficult since several tubes can grow from a single catalyst metal nanoparticle. Catalyst patterning has been used to reduce the density of the overall forest, producing alternating areas with higher or lower CNT density. A direct method of tracing whether a nanotube array structure follows the Wenzel or Cassie wetting regime has been developed using Ag nanoparticles as tracing agents [50]. Silver nanoparticles in a carrier solution wetting a nanostructured substrate will concentrate either inside the tubes or between them. In the Wenzel regime, upon removal of the carrier fluid the nanoparticles will move with the fluid, leaving the surface clean. In the Cassie regime, on the other hand, the fluid removal will leave behind a significant number of particles, leaving a trace that can be picked up with simple analytical techniques. This model has been successfully validated on superhydrophobic CNT forests, where the fluid removal was obtained by tilting the substrate until the liquid droplet slid away and using SEM to evaluate the residual concentration of Ag nanoparticles.

The wetting behaviour of TiO_2 nanotubes arrays is of primary importance to increase the efficiency of dye-sensitised solar cell applications, where maximizing the contact area between the dye and the tubes can lead to an increase in the solar conversion efficiency. A common technique to increase the wettability of the TiO_2 arrays by the dyes is UV irradiation. As an example, wetting of titania nanotube forests by aqueous electrolytes has been tested before and after UV irradiation showed that the UV irradiated tubes filled more readily. [51]. To precisely determine the depth of penetration inside the tubes a Pb marker was used to measure the penetration depth directly from cross-sectional SEM images after TiO_2 nanotubes were soaked for different times in a 1 M $Pb(NO_3)_2$ solution, with and without illumination. Short soaking time did not produce any significant filling without illumination and 24 h hours were required to obtain about 70% filling along the length of the tubes. On the other hand, nearly completely filled tubes were obtained after 1 hour after UV irradiation.

The hydrophilicity of as-formed titania nanotube arrays has also been verified using ionic liquid micro-droplets in the SEM [52]. A more hydrophobic behaviour, on the other hand, was obtained after coating the array with octadecyl silane with the contact angle in the 120-130˚ range. Interestingly, a ~40% reduction in the contact angle was obtained after exposure for up to 100 min to the electron beam. This effect can be easily explained by the formation of radicals on the substrate surface as it occurs in the case of UV irradiation. Superhydrophilic and superhydrophobic regions on titania arrays have been obtained using common microfabrication techniques [53]. First, using a photomask, UV irradiation was applied to selected regions of the array to increase locally the hydrophilicity. Second, modification of the non-irradiated areas with a fluorosilane induced a localized superhydrophobic behaviour (with contact angles up to 156º). The quality of the separation between the two regions was verified by preferential electrochemical deposition of octacalcium phosphate (OCP) nanocrystals on the hydrophilic regions. This technique has promising applications in bio-compatible coatings where drugs could be encapsulated in specific areas of the coating using simple microfabrication methods.

Carbon nanotube forests have been used as templates to grow hematite (α-Fe_2O_3) nano-chain arrays with a contact angle for water close to 0˚ [54]. The combination of a low contact angle and magnetic properties might lead to their use as filters to capture magnetic and paramagnetic micro- and nano-contaminants in waste water.

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Carbon nanotube forests have also proven attractive as gas diffusion layers. In one example, a CNT forest was grown over macro-porous carbon paper substrates [55]. These layers have been used in proton exchange membrane fuel cells to improve the selective diffusion of reactant gases to and water from the reaction zone, as well as providing electrical and mechanical support to the whole membrane electrode assembly. Contact angle measurements on these composite films showed a water contact angle as high as 168°, well above values for currently used PTFE-treated carbon paper, thereby improving diffusion selectivity. Similar results were obtained by a second group of researchers by growing CNTs on macro-porous, non-woven fibrous carbon paper, with a contact angle as high as 150º [56].

6 Conclusions

Wetting studies inside and outside nanotubes, nanochannels and nanotube arrays represent a research area that continues to attract substantial interest for both fundamental science and applications. The authors believe that there is scope for further growth of the area as there are a number of interesting topics that deserve further research. A first one is developing a theoretical framework for wetting inside nanoscale structures, linking wetting properties (contact angle, surface chemistry, surface structure, roughness, etc) to flow behaviour through such structures. Further investigation of the effect of nanoscale confinement on surface tension of liquids as well as the nature an magnitude of the line tension are also necessary to complete the theoretical picture. Such a model would also have a substantial impact on novel carbon-nanotube membranes being currently tested for water filtration and desalination, providing an explanation for the higher than expected flow rates observed through CNTs.

Another substantial area of research is the interaction of dyes with photoactive nanotubes, TiO_2, ZnO, etc, for dye-sensitized solar cells. Nanotube arrays are quickly replacing colloidal solutions of the particle due to higher surface area as well as providing a more direct path for charges to close the circuit. In order to deliver the promised increases in efficiency, better filling (and wetting) of the tube arrays by the dyes is necessary. Similarly, a better understanding of alumina nanoporous membranes would be beneficial to their use as templates for polymeric materials, where viscosity effects play a major role in determining the final quality of the nanostructured materials.

A third major area of research concerns nanotube arrays for superhydrophobic structures. With the theoretical framework in this area being quite clear, efforts are now concentrated on improving stability of superhydrophobic properties and tailoring of the adhesion properties. In the authors' opinion, this is the research area closest to delivering commercial applications, if production costs can be brought in line with well known hydrophobic (but not superhydrophobic) materials such as PTFE. Dynamic switching between a wetting and non-wetting state is also the object of intense research, where electrowetting is an established means to induce the change.

In conclusion, this is an exciting area of research with major possibilities of producing novel research and achieving scientifically and commercially significant results.

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Draft – please refer to published article only for details and data

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7 References:

1. Dujardin, E., et al., *Capillarity and Wetting of Carbon Nanotubes.* Science, 1994. **265**: p. 1850.

2. Ugarte, D., et al., *Filling carbon nanotubes.* Appl. Phys. A., 1998. **67**: p. 101-105.

3. Mattia, D. and Y. Gogotsi, *Review: static and dynamic behavior of liquids inside carbon nanotubes.* Microfluidics and Nanofluidics, 2008. **5**(3): p. 289-305.

4. Whitby, M. and N. Quirke, *Fluid Flow in Carbon Nanotubes and Nanopipes.* Nature Nanotechnology, 2007. **2**: p. 87-94.

5. Li, Y., J. Xu, and D. Li, *Molecular dynamics simulation of nanoscale liquid flows.* Microfluidics and Nanofluidics, 2010.

6. Starov, V.M., M.G. Velarde, and C.J. Radke, *Wetting and Spreading Dynamics.* Surfactant Science Series. 2007, BOca Raton, FLorida: CRC Press.

7. Barberis, F. and M. Capurro, *Wetting in the nanoscale: A continuum mechanics approach.* Journal of Colloid and Interface Science, 2008. **326**(1): p. 201-210.

8. Tavana, H. and A.W. Neumann, *Recent progress in the determination of solid surface tensions from contact angles.* Advances in Colloid and Interface Science, 2007. **132**(1): p. 1-32.

9.* Rossi, M.P., Y. Gogotsi, and K.G. Kornev, *Deformation of Carbon Nanotubes by Exposure to Water Vapor.* Langmuir, 2009. **25**(5): p. 2804-2810.

10. Bahrami, A.H. and M.A. Jalali, *Nanoscopic spontaneous motion of liquid trains: Nonequilibrium molecular dynamics simulation.* The Journal of chemical physics, 2010. **132**(2): p. 024702.

11. Chibbaro, S., et al., *Hydrokinetic simulations of nanoscopic precursor films in rough channels.* Journal of Statistical Mechanics-Theory and Experiment, 2009.

12. van Honschoten, J.W., N. Brunets, and N.R. Tas, *Capillarity at the nanoscale.* Chemical Society Reviews, 2010. **39**(3): p. 1096-1114.

13.** Nikolov, A., K. Kondiparty, and D. Wasan, *Nanoparticle Self-Structuring in a Nanofluid Film Spreading on a Solid Surface.* Langmuir, 2010. **26**(11): p. 7665-7670.

14. Derjaguin, B.V., N.V. Churaev, and V.M. Muller, *Surface Forces.* 1987: Consultants Bureau/Plenum Publishing Co.

15. Grzelak, E.M. and J.R. Errington, *Nanoscale Limit to the Applicability of Wenzel's Equation.* Langmuir, 2010. **26**(16): p. 13297-13304.

16. Lauga, E., M.P. Brenner, and H.A. Stone, *Microfluidics: The No-Slip Boundary Condition*, in *Handbook of Experimental Fluid Dynamics*, J. Foss, C. Tropea, and A. Yarin, Editors. 2005, Springer: New York.

17.** Joseph, S. and N.R. Aluru, *Why Are Carbon Nanotubes Fast Transporters of Water?* Nano Letters, 2008. **8**(2): p. 452-458.

18. Brenner, M.P. and D. Lohse, *Dynamic Equilibrium Mechanism for Surface Nanobubble Stabilization.* Physical Review Letters, 2008. **101**(21): p. 214505.

19. Suk, M.E., A.V. Raghunathan, and N.R. Aluru, *Fast reverse osmosis using boron nitride and carbon nanotubes.* Applied Physics Letters, 2008. **92**(13): p. 133120-3.

20. Fornasiero, F., et al., *Mechanism of Ion Exclusion by Sub-2nm Carbon Nanotube Membranes.* Materials Research Society, 2008. **1106**: p. Materials Research Society.

21. Holt, J.K., *Carbon Nanotubes and Nanofluidic Transport.* Adv. Mater., 2009. **21**(35): p. 3542–3550.

22. Whitby, M., et al., *Enhanced Fluid Flow through Nanoscale Carbon Pipes.* Nano Letters, 2008. **8**(9): p. 2632-2637.

23. Whitby, M., et al., *Erratum: Enhanced Fluid Flow through Nanoscale Carbon Pipes (2009) 9:7 (2802) 10.1021/nl900746g) (Additions & Corrections).* Nano Letters, 2009. **9**(7): p. 2802-2802.

24.* Thomas, J. and A.J.H. McGaughey, *Reassessing fast water transport through carbon nanotubes.* Nano Letters, 2008. **8**(9): p. 2788-2793.

25. Thomas, J., A.J.H. McGaughey, and O. Kuter-Arnebeck, *Pressure-driven water flow through carbon nanotubes: Insights from molecular dynamics simulation.* International journal of thermal sciences, 2010. **49**(2): p. 281-289.

15

26.*   Won, C.Y. and N.R. Aluru, *Structure and Dynamics of Water Confined in a Boron Nitride Nanotube.* American Chemical Society, 2008 **112**(6): p. 1812-1818.

27.   Hilder, T.A., D. Gordon, and S.H. Chung, *Salt Rejection and Water Transport Through Boron Nitride Nanotubes.* Small, 2009. **5**(19): p. 2183-2190.

28.   Wang, L. and Q. Ni, *A reappraisal of the computational modelling of carbon nanotubes conveying viscous fluid.* Mechanics research communications, 2009. **36**(7): p. 833-837.

29.   Insepov, Z., D. Wolf, and A. Hassanein, *Nanopumping Using Carbon Nanotubes.* NANOLETTERS, 2006. **Vol. 6**: p. 1893-1895.

30.   Gong, X., et al., *A charge-driven molecular water pump.* Nat Nano, 2007. **2**(11): p. 709-712.

31.   Wong-ekkabut, J., et al., *Static charges cannot drive a continuous flow of water molecules through a carbon nanotube.* Nat Nano, 2010. **5**(8): p. 555-557.

32.*   Horsch, M., et al., *Contact Angle Dependence on the Fluid-Wall Dispersive Energy.* Langmuir, 2010. **26**(13): p. 10913-10917.

33.   Chai, J., S. Liu, and X. Yang, *Molecular dynamics simulation of wetting on modified amorphous silica surface.* Applied surface science, 2009. **255**(22): p. 9078-9084.

34.   Kuang, C. and G. Wang, *A novel far-field nanoscopic velocimetry for nanofluidics.* Lab on a chip, 2010. **10**(2): p. 240-245.

35.*   Tran, M.Q., et al., *Direct Measurement of the Wetting Behavior of Individual Carbon Nanotubes by Polymer Melts: The Key to Carbon Nanotube-Polymer Composites.* Nano Letters, 2008. **8**(9): p. 2744-2750.

36.   Bazilevsky, A.V., et al., *Room-temperature, open-air, wet intercalation of liquids, surfactants, polymers and nanoparticles within nanotubes and microchannels.* Journal of Materials Chemistry, 2008. **18**: p. 696–702.

37.   Kong, J., et al., *Enhanced Polymer Melts Flow through Nanoscale Channels under Vibration.* Journal of Physical Chemistry C, 2009. **113**(2): p. 624-629.

38.   Insepov, Z., D. Wolf, and A. Hassanein, *Nanopumping Using Carbon Nanotubes.* Nano Letters, 2006. **6**(9): p. 1893-1895.

39.   Kim, P., et al., *Multi-curvature liquid meniscus in a nanochannel: Evidence of interplay between intermolecular and surface forces.* Lab on a Chip, 2009. **9**(22): p. 3255-3260.

40.   Dimitrov, D.I., A. Milchev, and K. Binder, *Molecular dynamics simulations of capillary rise experiments in nanotubes coated with polymer brushes.* Langmuir, 2008. **24**(4): p. 1232-1239.

41.   Liu, M., et al., *Tailoring the wettability of polypropylene surfaces with halloysite nanotubes.* Journal of colloid and interface science, 2010. **350**(1): p. 186-93.

42.   Wu, T., Y. Pan, and L. Li, *Study on superhydrophobic hybrids fabricated from multiwalled carbon nanotubes and stearic acid.* Journal of colloid and interface science, 2010. **348**(1): p. 265-70.

43.   Yun-Ze, L., et al., *Electrical, dielectric and surface wetting properties of multi-walled carbon nanotubes/nylon-6 nanocomposites.* Chinese physics B, 2009. **18**(3): p. 1221-1226.

44.   Qian, H., et al., *Carbon nanotube grafted carbon fibres: A study of wetting and fibre fragmentation.* Composites. Part A, Applied science and manufacturing, 2010. **41**(9): p. 1107-1114.

45.   Sato, H. and M. Sano, *Characteristics of ultrasonic dispersion of carbon nanotubes aided by antifoam.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008. **322**(1-3): p. 103-107.

46.   Li, Y.-F., et al., *Electromagnetic modulation of carbon nanotube wetting.* Journal of Materials Chemistry, 2009. **19**(41): p. 7694-7697.

47.   Cho, W.K. and I.S. Choi, *Fabrication of Hairy Polymeric Films Inspired by Geckos: Wetting and High Adhesion Properties.* Advanced Functional Materials, 2008. **18**(7): p. 1089–1096.

48.   Lai, Y., et al., *Electrophoretic deposition of titanate nanotube films with extremely large wetting contrast.* Electrochemistry communications, 2009. **11**(12): p. 2268-2271.

49.   Jung, Y. and B. Bhushan, *Dynamic effects of bouncing water droplets on superhydrophobic surfaces.* Langmuir, 2008. **24**(12): p. 6262-6269.

50.   Wang, K., et al., *Direct Method of Tracing the Wetting States on Nanocomposite Surfaces.* Langmuir, 2010. **26**(11): p. 7686-7689.

51.   Kim, D., et al., *Capillary effects, wetting behavior and photo-induced tube filling of TiO2 nanotube layers.* Nanotechnology, 2008. **19**(30).

52.*   Roy, P., T. Dey, and P. Schmuki, *Scanning Electron Microscopy Observation of Nanoscopic Wetting of TiO2 Nanotubes and ODS Modified Nanotubes Using Ionic Liquids.* Electrochemical and solid-state letters, 2010. **13**(7): p. E11-E13.

16

53.   Lai, Y., et al., *Selective formation of ordered arrays of octacalcium phosphate ribbons on TiO(2) nanotube surface by template-assisted electrodeposition.* Colloids and Surfaces B: Biointerfaces, 2010. **76**(1): p. 117-22.

54.   Lu, H.B., et al., *Hematite nanochain networks: Simple synthesis, magnetic properties, and surface wettability.* American Institute of Physics, 2008. **92**.

55.   Stuckey, P., et al., *Gas Diffusion Layers for Proton Exchange Membrane Fuel Cells Using In situ Modified Carbon Papers with Multi-walled Carbon Nanotubes Nanoforest.* Fuel cells, 2010. **10**(3): p. 369-374.

56.   Kannan, A.M., P. Kanagala, and V. Veedu, *Development of carbon nanotubes based gas diffusion layers by in situ chemical vapor deposition process for proton exchange membrane fuel cells.* Journal of power sources, 2009. **192**(2): p. 297-303.