CARBON NANOTUBE BASED FUNCTIONAL SUPERHYDROPHOBIC COATINGS

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ABSTRACT

The main objective of this dissertation is synthesis of carbon nanotube (CNT) based superhydrophobic materials. The materials were designed such that electrical and mechanical properties of CNTs could be combined with superhydrophobicity to create materials with unique properties, such as self-cleaning adhesives, miniature floatation devices, ice-repellant coatings, and coatings for heat transfer furnaces. The coatings were divided into two broad categories based on CNT structure: Vertically aligned CNT arrays (VA coatings) and mesh-like (non-aligned) carbon nanotube arrays (NA coatings).

VA coatings were used to create self-cleaning adhesives and flexible field emission devices. Coatings with self cleaning property along with high adhesiveness were inspired from structure found on gecko foot. Gecko foot is covered with thousands of microscopic hairs called setae; these setae are further divided into hundreds of nanometer sized hairs called spatulas. When gecko presses its foot against any surface, these hairs bend and conform to the topology of the surface resulting into very large area of contact. Such large area of intimate contact allows geckos to adhere to surfaces using van der Waals (vdW) interactions alone. VA-CNTs adhere to a variety of surfaces using a similar mechanism. CNTs of suitable diameter could withstand four times higher adhesion force than gecko foot. We found that upon soiling these CNT based adhesives (gecko tape) could be cleaned using a water droplet (lotus effect) or by applying vibrations. These materials could be used for applications requiring reversible adhesion.
VA coatings were also used for developing field emission devices. A single CNT can emit electrons at very low threshold voltages. Achieving efficient electron emission on large scale has a lot of challenges such as screening effect, pull-off and lower current efficiency. We have explored the use of polymer-CNT composite structures to overcome these challenges in this work.

NA-CNTs were used to create stable superhydrophobic coatings on steel. As compared to VA-CNT, mesh-like structures could sustain large thermal and mechanical stresses without loosing their superhydrophobic properties. A process was developed to reinforce these coatings using an elastomer. Floatation behavior of these coatings was tested. When pressed on water surface, a large hydrostatic pressure acts on the coatings. Optimized mesh-like structures had a very high stability and were important in creating these floatation devices. NA coatings on steel were also used for increasing heat transfer efficiency of heat transfer furnaces. CNTs are known to have two orders of higher conductivity than copper. When combined with superhydrophobicity, these coatings could be used for efficient heat transfer. Stainless steel pipes coated with these coatings were demonstrated to have higher thermal transfer properties as compared to uncoated pipes.
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1.1 Motivation

Superhydrophobicity is an important property which finds application in self-cleaning surfaces, micro-fluidics, filtration, robotics and naval applications [1-5]. Hydrophobicity means fear (phobic) of water (hydro). Traditionally surfaces which show water contact angle of greater than 90° are considered hydrophobic. Superhydrophobicity is the special case of hydrophobic surfaces where water contact angle is greater than 150°. Many examples of superhydrophobic surfaces are found in nature. One of the most studied superhydrophobic surfaces in nature is lotus leaf [6-10]. Superhydrophobicity helps lotus leaf to stay clean. Water would bead up on lotus leaf and roll off, carrying dirt particles with it. This phenomenon is termed as self cleaning or lotus effect. In other natural systems, superhydrophobicity may play different roles e.g. in legs of water striders, superhydrophobicity help them to stand on surface of water [11-12]. Synthetic superhydrophobic surfaces are used for many purposes, e.g. for creating self cleaning surfaces and controlling flow in micro-fluidic devices. These synthetic superhydrophobic surfaces are generated by controlling the chemistry and morphology of surfaces. Low energy organic molecules like fluorinated molecules and waxes are used to control the chemistry of these surfaces. Techniques like electro-spinning, casting, and lithography are used to create surfaces with high roughness [13-20]. Even though these surfaces show
very high water contact angle, yet use of organic molecules limits their use in applications requiring conductivity and high temperature applications. Recently many carbon-nanotubes (CNT) based structures coated with fluorinated molecules are shown to be superhydrophobic [21-24]. CNT have high conductivity and thermal stability and can help in creating conductive superhydrophobic coatings. Yet, coating CNT arrays by organic molecules may lead to loss of such properties. The second disadvantage of such systems is that they may have low mechanical and hydrostatic stability.

The current work was inspired from the need to create stable superhydrophobic surfaces using CNT. The surface created was such that the properties of individual CNT could be harnessed. This would help us create superhydrophobic surfaces with unique functional properties. CNT arrays with different geometries were grown using chemical vapor deposition – floating-catalyst process. The process allowed us to create large areas of uniform CNT structures. The process allows us to coat inaccessible surfaces, like inner surfaces of pipes. These arrays showed very high water contact angle without any external coatings due to highly porous structure. These coatings were further reinforced by partially trapping the CNT structures in polymer matrix. The process was designed such that it would impart stability to the structures, without affecting their superhydrophobic behavior and conductivity. It was shown that such system could be used to form novel materials with unique properties, e.g. self cleaning adhesives, flexible electron emitters, miniature floatation devices and self cleaning and anti-icing coatings.
1.2 Thesis overview

The thesis has been divided in five Chapters. Chapter-II of the thesis gives theoretical background and is divided into four sections: CNT, wetting, adhesion and electron-emission. The section on CNT includes information on structure, properties and how CNT are synthesized. The section on wetting gives theoretical background on wetting behavior and physics behind superhydrophobicity. The third section talks about various mechanisms of adhesion. How viscoelastic materials adhere to different surfaces. It describes fibrillar adhesives, as seen in nature and how such systems can impart self-cleaning ability to the adhesives. The fourth section gives theoretical background of electron emission from surfaces. It discusses a few examples of electron emitting devices formed using CNT.

Chapter III describes vertically aligned coatings formed using CNT. The process of incorporation of CNT in polymer matrix and various attributes of these coatings are discussed. The Chapter talks about how self cleaning adhesives and flexible field emission devices were formed using aligned nanotube-polymer systems. Chapter IV talks about mesh-like CNT coatings on stainless steel substrate. The section talks about various applications developed based on superhydrophobic steel surfaces. The last Chapter, Chapter V gives the summary of the work and conclusion.
CHAPTER II
BACKGROUND

2.1 Carbon-Nanotube

Carbon nanotubes (CNT) are sheets of graphite rolled into cylindrical shape. These can be single-walled CNT (SWCNT) or multi-walled CNT (MWCNT) [25-26].

2.1.1 Structure and properties

Carbon atoms in CNT are sp2 bonded and form three \( \sigma \) bond and one \( \pi \) bond. The \( \sigma \) bond in CNT is responsible for their high modulus. The \( \pi \) bond consists of delocalized \( \pi \) electrons. Due to conjugation in the system, \( \pi \) electrons can carry current along CNT length, thus accounting for their electronic properties. The ends of CNT are capped with fullerene type structures [27]. Figure 2-1 shows a sketch of SWCNT. Diameter of SWCNT may vary from a few angstroms to a few nanometers (nm). MWCNT are composed of many concentric SWCNT. The diameter of innermost tube in MWCNT is of the order of few nm, whereas outermost tubes maybe as big as 40 to 50 nm in diameter. The separation between two such concentric cylinders in a MWCNT is 3.45 Å [28]. This value is close to 3.337 Å for interlayer separation in graphite.
Figure 2.1: Structure of single walled carbon nanotube (SWCNT) [29]. CNT is composed of hexagonally bonded carbon atoms. The ends of nanotubes are capped with fullerene rings.

There can be more than one way in which a graphene sheet can be rolled up to form SWCNT. Therefore SWCNT with different helicities are observed. To illustrate this, let’s consider a graphene sheet as shown in Figure 2.2. The helicity of CNT structure can be defined by two quantities, (a) Chiral angle ($\theta$) and (b) chiral vector ($C_h$) [30]. The chiral vector is a line that connects two crystallographically equivalent sites on a 2D graphene sheet. The angle that it makes with the zig-zag direction gives chiral angle (it can have a maximum value of 30°). The chiral vector can be defined in terms of unit vectors in a 2D graphene lattice as shown by $a_1$ and $a_2$ in Figure 2.2 [31].

$$C_h = na_1 + ma_2$$  \hspace{1cm} (2.1)

Where $n$ and $m$ are integers.
Many possible chiral vectors can be specified depending on the value of \( n \) and \( m \). Two limiting cases are zig-zag tubes and armchair tubes. Zig-zag tubes are given by \( n \neq 0 \) and \( m = 0 \), \( (\theta = 30^\circ) \) and armchair tubes are given by \( n = m \neq 0 \), \( (\theta = 0^\circ) \) \[33\]. The integers \( n, m \) can be used to determine diameter and chiral angle of CNT using following equations:

\[
d = \frac{a\sqrt{m^2 + mn + n^2}}{\pi} \quad (2.2)
\]

\[
\theta = \arctan\left(\frac{-\sqrt{3}m}{2n + m}\right) \quad (2.3)
\]
Since CNT derive their electrical properties from delocalized π-electrons, bond-deformations effects electronic properties. It has been observed that SWCNT may be metallic or semi-conducting depending on their chirality. If the chiral vector n, m are such that (n - m) is a multiple of three, then SWCNT would be metallic, else it would be semi-conducting. Scanning Tunneling Microscope (STM) has been used for exploring local electronic properties of CNT [34]. It was seen that conductivity and band gap along the length of CNT can vary. Such behavior may arise due to the defects in the structure. Metallic SWCNT have a 1-D structure, this leads to ballistic transport of electrons. These nanotubes can carry $10^9$ A/cm$^2$ current with no heating [35].

Electronic properties of MWCNT are different from SWCNT. MWCNT are formed of many concentric nanotubes. About 1/3 of these nanotubes are metallic with large interlayer capacitance. This capacitance connects these concentric tubes to each other resistively and inductively [36]. For a dc current, only the outermost layer may take part in conduction, but for high frequency current, all the layers participate in conduction. In case of MWCNT, total electron-density is proportional to the number of metallic layers [37]. Being a 1-D electron system, it was predicted that CNT may behave as Luttinger liquids [38]. Electronic properties of single CNT have been determined experimentally using AFM and STM. It was observed that at low voltages the tunneling conductance obeys non-Ohmic power law, which is predicted both by the Luttinger liquid and the Environment-Quantum-Fluctuation theories. However, at higher voltages there is a crossover to Ohm’s law with a Coulomb-blockade offset, which agrees with the Environment-Quantum-Fluctuation theory, but cannot be explained by the Luttinger-
liquid theory [39-41]. In addition to hexagons, CNT can have pentagons and heptagons in their structure. Presence of pentagons and heptagons may lead to bent CNT. These defects largely affect electrical and chemical properties of CNT [42].

CNT derive their mechanical properties from $\sigma$ bonds and $\pi$ bonds. They have strength to weight ratio higher than that of steel. The reason for the strength of CNT in the axial direction is the sp2 bonds within the graphite sheets. Since SWNT are made of single-rolled graphene sheets, they are ideal graphite fibers in terms of elastic properties [43-45]. It was shown using Raman spectroscopy that CNT can sustain their structure even in pressures up to 30 GPa. Young’s modulus of SWNT has been calculated theoretically to be greater than 1 TPa. This comes in good agreement with the experimental values. In another experimental measurement, Young’s modulus of CVD produced MWNT was measured to be lower than 100 GPa [46]. The main reasons for such differences in strength are due to defects within the graphite planes and misalignment of the graphitic planes with regard to the central axis. Falvo et al. [47] used AFM tip to study flexural rigidity of CNT (CNT). It was observed that (CNT) could be bent through large angles without any damage. They showed that MWCNT can sustain local strain as high as 16% without failing.

2.1.2 Synthesis

Many techniques are used for growing CNT, like laser ablation, arc discharge and chemical vapor deposition (CVD). In laser ablation method metal catalyst containing graphitic targets are irradiated with high energy laser beams, e.g. CO$_2$ laser [48]. The power of laser may be as high as 2 kW. Laser ablation techniques help in continuous
production of CNT at high rates. Arc discharge method may produce CNT at lesser cost [49]. The method involves generating an electric arc between two electrodes. One of these electrodes is graphite and other electrode maybe combination of graphite and metal catalyst system. For the current work CVD technique was used so it would be described in detail.

In CVD process for growth of CNT, a carbon source is introduced in a furnace at temperatures ranging from 600°C to 1100°C in argon, hydrogen atmosphere in presence of a metal catalyst [50]. At high temperatures and in presence of catalyst particles, the carbon source is thermally decomposed into smaller segments and gets absorbed onto the metal particles forming an alloy. Once the metal gets saturated with carbon, nanotubes are extruded from it. This mechanism of growth of CNT is also known as Vapor-Liquid-Solid (VLS) growth mechanism [51-53]. The VLS growth mechanism is shown in the Figure 2.3.
Figure 2.3: Vapor-Liquid-Solid growth process. (A) At high temperatures, metal nanoparticles melt and carbon source decomposes. This decomposed carbon vapors diffuse into the metal catalyst. (B) This diffused carbon forms alloy with the metal catalyst. At a point, metal catalyst gets saturated with carbon source. (C) and (D) show two mechanisms by which nanotubes get extruded from the metal nanoparticles. The name of these two processes is based on where the catalyst particle sits on the carbon nanotube. If the catalyst particle is on top of CNT as shown in (C) it is called tip growth mechanism. If the catalyst particle is at the root of CNT, as shown in (D) it is called root growth mechanism.

For CNT growth, two kind of CVD process are used. One is called floating-catalyst method. In this technique the metal catalyst is dissolved in the carbon source. This metal catalyst may be an organo-metallic compound like a metallocene (e.g. ferrocene). This mixture of carbon source and metal catalyst is then evaporated and introduced in the CVD furnace. Second mechanism involves depositing of the metal
catalyst on the substrate under suitable condition. The carbon source is then introduced in the CVD furnace at appropriate pressure. The most common carbon source used for growth of CNT are, acetylene, xylene, ethylene and ethanol, though many other systems maybe used.

The catalysts particles used for growth of CNT are generally based on three transition metals: Fe, Co or Ni. Both the electronic configuration and physical form of these metals is important for their role as catalyst. The electronic configuration of these metals is Fe ([Ar]4s² 3d⁶), Co ([Ar]4s² 3d⁷), Ni ([Ar]4s² 3d⁸). All these elements have vacant d-orbital. This is essential for their role in growth of CNT. The energy of these vacant d-orbital is such that they can overlap with π-electrons of sp² bonded carbon atoms. In case of Fe (1;1, 0) plane and in case of Co and Ni, (1, 1, 1) planes have suitable symmetry and distances, that is required to overlap with the lattice of a graphene sheet. Under high temperature and in presence of carbon source, these metals particles undergo calcination process. This leads to formation of metal nanoparticles. Carbon gets diffused in these metal nanoparticles, forming an alloy and CNT are grown from that alloy structure [54-57].

For growth of aligned CNT by floating catalyst method, it is essential to choose the right kind of substrate, in addition, to choosing the right catalyst and carbon source. It was shown by Zhang, et. al that when Si and SiO₂ surfaces were exposed to ferrocene, it was adsorbed selectively on SiO₂ [58]. Therefore CNT could be grown on SiO₂ substrate but not on Si substrates. The other parameters important for substrate are that it should have sufficiently high melting point. It has been shown that CNT can be grown on a variety of other substrates using CVD process.
CVD process of growing CNT is the most versatile method. It allows coating CNT on different substrates. Using CVD process one can grow aligned CNT or micropatterned CNT, which are essential for CNT based electronics. CVD process can be scaled up and recently, a letter sized sheet of aligned CNT was grown using this method [59]. The disadvantage of CVD process is that it has low activity of the catalyst. Only a small fraction of catalyst actually takes place in reaction. It was suggested in earlier work that the catalyst particles get coated with amorphous carbon over period of time. This renders catalyst particle inactive. If a small amount of weak oxidizing agent is added in the furnace, it could remove the amorphous carbon and enhance activity of catalyst. This is a very important step because it will not only help in more economical growth of CNT but the resulting CNT will have less impurities. Based on this hypothesis Ijima, developed water assisted CVD growth process called super CVD [60-62]. In super growth CVD process, the activity of catalyst is enhanced by addition of small amount of water in the CVD furnace. In super CVD growth process, it was seen that the efficiency was two orders of magnitude higher than normal growth process.

Recently it has been reported that ceramic catalyst particles can be used in place of transition metal catalysts. Steiner et. al. used ZrO$_2$ as a catalyst for growth of both multi-walled and single-walled CNT [63]. This discovery opens up new questions on mechanism of carbon nanotube growth.
2.2 Wetting

Wetting can be defined as ability of a liquid to spread on a solid substrate. The degree of spread depends on cohesive forces between liquid molecules and adhesive interactions between liquid and solid. The resultant of these adhesive and cohesive forces causes liquid to take an equilibrium shape on solid substance, which is defined by contact angle of liquid on solid [64]. Wetting behavior of different liquids forms an important part of biological and engineering systems. In the following section physics behind wetting properties of various solid-liquid systems would be discussed. A special case of wetting – superhydrophobicity, would be discussed in detail at the later part of the section.

2.2.1 Surface tension

Surface tension is force acting on liquid surface due to attractive intra-molecular forces (cohesive force). In liquid bulk these attractive interactions act from all sides on the liquid molecule but on surface these interactions are absent on surface-air interface. This causes an enthalpic penalty for molecules on surface. This enthalpic penalty is proportional to the strength of bonds between liquid molecules. The units of surface tension are force per unit length or energy per unit area and will be depicted by symbol $\gamma$ [65-68]. This effect could be depicted by following diagram:
Figure 2.4: Cohesive forces in liquid. The above diagram shows forces on a liquid molecule in bulk and a liquid molecule on surface. The liquid molecule is depicted by grey and black circle and arrows around it show attractive forces acting on it. In bulk the liquid molecules experience interactive interactions from all sides. On the surface these attractive interactions are absent from one side.

Due to surface-tension force, liquids like to reduce their surface area to as less as possible and form spherical droplets. But when a liquid droplet comes in contact with a solid surface, (a) Solid-liquid surface is formed; (b) Solid-air surface is lost and (c) Liquid vapor interface changes. Depending on these interactive forces the liquid may change its shape. The angle that the liquid droplet subtends at solid-liquid interface is known as water contact angle. This behavior of liquid on solid surface will depend on surface energy of solid, surface tension of liquid and solid liquid interactions.
2.2.2 Contact angle

The angle that a liquid droplet subtends at solid/liquid/vapor triple point is known as contact angle of liquid on the given solid surface [69]. Figure 2.5 shows a sketch of liquid droplet on solid surface; the contact angle is depicted by $\theta$.

![Contact angle diagram](image)

Figure 2.5: Contact angle of liquid on solid surface. The above sketch shows a liquid droplet sitting on a solid surface forming a contact angle $\theta$. The equilibrium contact angle depends on the forces acting on the liquid droplet due to its interaction with solid substance and its surface tension. $\gamma_{sl}$ denotes force due to solid liquid interaction. $\gamma_{sv}$ denotes force due to solid vapor interaction or surface energy of solid surface. $\gamma_{lv}$ denotes force due to liquid vapor interaction (surface tension of liquid).

The equilibrium contact angle $\theta$ of a liquid droplet on a solid surface was derived based on solid-liquid, solid-vapor and vapor-liquid interactions and is known as Young’s equation [70]. It is given by following expression:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$  \hspace{1cm} (2.4)

For a given solid surface, liquid with higher surface tension would form higher contact angle as compared to liquid with lower surface tension. For case where the liquid
is water, solids are classified as hydrophobic (water repelling) or hydrophilic (water loving). The materials on which water shows contact angle $\theta < 90^\circ$ are considered hydrophilic and materials showing $\theta > 90^\circ$ are considered hydrophobic [71].

Another important parameter describing liquid-solid interactions is contact angle hysteresis. Contact angle hysteresis is the difference in advancing and receding contact angle of liquid just before it starts sliding (sliding angle) [73-75] as shown in Figure 2-6. Contact angle hysteresis indicates ease with which water droplet can roll down the surface of solid. There is no direct relationship between contact angle and contact angle hysteresis of water droplets on different surfaces. It has been observed that surfaces with high contact angle may have higher contact angle hysteresis than surfaces with lower contact angle and vice-versa. The main reasons for contact angle hysteresis are molecular inhomogeneity and pinning of water droplet at triple point due to adhesion hysteresis [76]. Designing surfaces with low contact angle hysteresis is important for applications like self-cleaning and micro-fluidics.
Wetting behavior of a solid surface can be controlled by controlling the chemistry of surface. Table 2.1 gives contact angles of water and an organic liquid (methyl iodide) on different polymer surfaces. From table 2.1 it can be observed that the surfaces which have lower surface energy form higher contact angle with water, e.g. Nylon 6,6 and poly (methylmethacrylate). However in case of poly(vinylidenefluoride) vs. poly(vinylchloride), water contact angle does not increase with decreasing surface energies. The reason behind such behavior is that surface energy component due to dispersive forces is higher in poly (vinylchloride) whereas in case of poly (vinylidenefluoride) even though the total surface energy is less but surface energy component due to H-bonding is higher. Such surfaces have favorable interactions with
water, hence lower water contact angle. Therefore, the wetting properties can be tailored by controlling the chemistry of solid surfaces.

Table 2.1: Surface energies of different polymer surfaces. The following table gives surface energies of different polymer surfaces and different components of their surface energy (dispersive (\(\gamma_{sd}\)) and hydrogen bonding (\(\gamma_{sH}\)). Contact angle of water and methyl iodide on these polymers is given [72].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(\gamma_{sd})</th>
<th>(\gamma_{sH})</th>
<th>(\gamma_s)</th>
<th>Water</th>
<th>Methyl Iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6,6</td>
<td>34.1</td>
<td>9.1</td>
<td>43.2</td>
<td>70</td>
<td>41</td>
</tr>
<tr>
<td>Poly (methylmethacrylate)</td>
<td>35.9</td>
<td>4.3</td>
<td>40.2</td>
<td>80</td>
<td>41</td>
</tr>
<tr>
<td>Poly (vinylidinechloride)</td>
<td>42.0</td>
<td>3.0</td>
<td>45.0</td>
<td>80</td>
<td>29</td>
</tr>
<tr>
<td>Poly (vinylfluoride)</td>
<td>31.3</td>
<td>5.4</td>
<td>36.7</td>
<td>80</td>
<td>49</td>
</tr>
<tr>
<td>Poly (vinylidinefluoride)</td>
<td>23.2</td>
<td>7.1</td>
<td>30.3</td>
<td>82</td>
<td>63</td>
</tr>
<tr>
<td>Poly (vinylchloride)</td>
<td>40.0</td>
<td>1.5</td>
<td>41.5</td>
<td>87</td>
<td>36</td>
</tr>
<tr>
<td>Poly (ethyleneterephalate)</td>
<td>37.8</td>
<td>3.5</td>
<td>41.3</td>
<td>81</td>
<td>38</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>41.4</td>
<td>0.6</td>
<td>42.0</td>
<td>91</td>
<td>35</td>
</tr>
<tr>
<td>Polyethylene (low density)</td>
<td>32.0</td>
<td>1.1</td>
<td>33.1</td>
<td>94</td>
<td>52</td>
</tr>
<tr>
<td>Poly (trifluoroethylene)</td>
<td>19.9</td>
<td>4.0</td>
<td>23.9</td>
<td>92</td>
<td>71</td>
</tr>
<tr>
<td>Poly (tetrafluoroethylene)</td>
<td>12.5</td>
<td>1.5</td>
<td>14.0</td>
<td>108</td>
<td>88</td>
</tr>
<tr>
<td>Paraffin</td>
<td>25.4</td>
<td>0.0</td>
<td>25.4</td>
<td>108</td>
<td>66</td>
</tr>
<tr>
<td>Fluorinated methacrylic polymer A</td>
<td>9.1</td>
<td>0.3</td>
<td>9.4</td>
<td>120</td>
<td>98</td>
</tr>
</tbody>
</table>
In the above table, \( \gamma \) denotes surface energy of the solid substrate. \( \gamma_{sd} \) is the surface energy component due to dispersive forces, \( \gamma_{H} \) is the surface energy component due to H-bonding component and \( \gamma_{s} \) is the total surface energy.

2.2.3 Superhydrophobicity

Superhydrophobicity is the special case of hydrophobic surfaces which show water contact angle of greater than 150°. From table 2.1 it can be see that with any known surface it is not possible to attain water contact angle of greater than 120°. However, in nature many superhydrophobic systems exist e.g. leaves of lotus plant, legs of water strider and lady mantle plant [10, 11, 77]. It has been observed that all these natural materials have multidimensional roughness on their surface. This roughness plays a very important role in determining contact angle of water on these materials. Young’s equation was derived assuming a smooth surface. But if the surface has roughness associated with it, the area of contact between the water droplet and surface may not be just the projected area. In case of rough surfaces, two kinds of situations might occur. In one case, water droplet may wet the whole area (Wenzel regime) and in other case water droplet may just be sitting on top of roughness with air trapped under it (Cassie regime).

Superhydrophobic surfaces where water wets the entire surface are described by Wenzel regime (This is called wetting state) [78]. The geometry of water droplet in Wenzel regime is shown in Figure 2.7.
Figure 2.7: Wenzel-regime. The above sketch shows water droplet sitting on a surface with square roughness. In this case the contact area between water droplet and solid surface is not just the projected area but is determined based on roughness of the material (shown by red line in the Figure).

Water contact angle in this case is given by Wenzel’s equation:

$$\cos \theta^* = r \cos \theta$$  \hspace{1cm} (2.5)

Where $\theta^*$ is the apparent contact angle on the textured surface, $r$ is the surface roughness and $\theta$ is the contact angle on smooth surface. In Wenzel state if the material is hydrophilic, it will become superhydrophillic and if it is hydrophobic it becomes superhydrophobic. In case of hydrophobic surfaces Wenzel regime may show high water contact angle, but due to pinning of water droplet at the roughness a very high sliding angle is observed [79-80]. Therefore, materials showing Wenzel behavior are not suitable for properties like self-cleaning.

Cassie regime is referred to state where a water droplet sits on top of the roughness, such that air is trapped under it. It is also known as composite state, since droplet is sitting on a composite structure. Cassie regime is shown schematically in Figure 2.8. In Cassie regime water contact angle is given by:

$$\cos \theta^* = -1 + \Phi s (1 + \cos \theta)$$  \hspace{1cm} (2.6)
Where, $\theta^*$ is water contact angle on surface, $\Phi_s$ is fraction of solid in contact with liquid and $\theta$ is Equilibrium contact angle on smooth surface [81-84].

Figure 2.8: Cassie-regime. In Cassie regime, the water droplet does not completely wets the solid substrate but sits on the roughness. This leads to air trapped between liquid droplet and solid surface.

In Cassie regime superhydrophobicity can be attained even if the surface is slightly hydrophilic. Since water is sitting on top of roughness, in Cassie regime, very small contact angle hysteresis is seen. Low contact angle hysteresis is important for many functional properties of superhydrophobic surfaces, like self-cleaning, floatation and ice-retardant coating. It was observed that the wetting state of a surface may undergo a transition from Cassie state to Wenzel state over a period of time [85-88]. Designing surfaces with stable Cassie regimes is very important for creating functional superhydrophobic surfaces (e.g. self-cleaning surfaces).

In all the natural surfaces like lotus leaf and water strider, it is seen that the surface has multidimensional roughness. Lotus leaf has two dimensional roughnesses. It has microscopic structures and those structures are composed of smaller hairy structures.
Such multi dimensional roughness is very important to achieve stable Cassie regime. The structure of lotus leaf is shown in Figure 2.9. Lotus leaf is composed on microscopic nodes which are further composed of smaller hairs. This two dimensional roughness is very important to achieve stable Cassie-regime. An example of multidimensional roughness is shown by a cartoon in Figure 2.10.

Figure 2.9: Lotus leaf. The above image shows a SEM micrograph of lotus leaf surface. It can be observed that the surface of lotus leaf has microscopic nodes. These nodes are further composed of sub-micron hairy structures [10].
2.3 Examples of synthetic superhydrophobic surfaces

Superhydrophobic surfaces are very important for a number of applications, therefore a large variety of techniques have been developed to create superhydrophobic surfaces. In the current section some of these structures would be discussed. All these techniques are based on using low energy molecules to create surfaces with high roughness. The most common polymers used for creating superhydrophobic surfaces are fluoro-polymers. These are attractive because of their low surface energy.

The most common and easy way to form a superhydrophobic surface is by casting. An example is shown in the following Figure. In this case Yabu et. al casted a thin film of fluorinated polymer from solution [89]. The resulting structure formed a transparent superhydrophobic film. Such technique is very useful for imparting self cleaning ability to see through glasses. The advantage of this process is its versatility. However it is challenging to form intricate multi-dimensional structures using casting.
Figure 2.11: Superhydrophobic surface created using casting. The above SEM image shows surface of a superhydrophobic surface created by solution casting. The left inset shows the chemical structure of molecule used to coat the template. The right inset shows water droplet sitting on the template. [89]

Another technique to create superhydrophobic surfaces that has been widely studied is electrospinning. Electrospinning yields structure formed of nanometer sized fibers. These fibers lay on top of each other to yield a highly porous structure, as shown in following Figure. By electrospinning a suitable polymer or coating electrospun fibers with some low energy molecules can yield to very high water contact angles [90].
Figure 2.12: Superhydrophobic surface created using electrospinning. The above SEM image shows an electrospun fiber mat. The fiber is a block co polymer, poly(styrene-b-dimethylsiloxane). The structure showed water contact angle of 163°. Such high contact angle is due to surface enrichment of low energy poly(dimethyl siloxane) and high roughness due to electrospun structure [90].

One of the most versatile techniques for creating superhydrophobic surfaces is photolithography. In photolithography technique a photo-resist polymer is coated on a substrate (e.g. silicon wafer). This photo-resist polymer is then cross-linked using a ultraviolet lamp. A mask is used so that only selective portions of photo-resist are cross-linked. The remaining portion is then removed by washing with suitable solvent. Silicon wafer, partially coated with photo-resist is then etched in acid. The portion of silicon wafer not covered with photo-resist gets etched, forming the desired pattern on silicon wafer. Multidimensional patterns can also be formed using photolithography technique. Current lithographic techniques based on electron beam etching can form nanometer sized patterns. Larger pattern sizes can be formed using less costly soft lithographic
techniques. The following Figure shown an example of pattern formed using photolithography:

![Superhydrophobic surface created using photolithography](image)

Figure 2.13: Superhydrophobic surface created using photolithography. The above SEM image shows pillar like structures formed using photolithography. [91]

The main drawback of photolithography is that it is a long and expensive process. Many other techniques of creating superhydrophobic surfaces are available. Most of these techniques are based on using organic molecules. Therefore these materials are thermal and electrical insulators. Carbon nanotube based superhydrophobic surfaces have been created by coating aligned nanotube structures with low energy molecules like poly(tetrafluoroethylene) [21-24]. Nanotube structure have inherent nano-scale roughness, when combined with low energy molecules, superhydrophobic surfaces with high hydrostatic stability can be synthesized. However, coating the CNT with fluorinated polymers is not desirable for many applications like for microelectronics and self-
cleaning adhesives. Another disadvantage of such process is that coating inaccessible surfaces, like inside surfaces of pipes is not feasible. The current techniques face challenge to attain superhydrophobicity using CNT without altering the surface chemistry.

2.4 Adhesion

Adhesion is an attractive interaction between two materials. Adhesion between two solid surfaces maybe attained by various means, like capillary-forces, chemical-bonding, mechanical-interlocking or electrostatic-interaction. Example of these forces is depicted in Figure 2.14.

Figure 2.14: Mechanisms of adhesion. The above sketch shows various mechanisms to adhere two surfaces together. (A) Adhesion due to capillary forces. (B) Adhesion using pressure difference. (C) Adhesion by mechanical interlocking. (D) Adhesion by electrostatic forces.
Most of the commercial adhesives available are based on viscoelastic materials. Such adhesives employ van der Waals interactions to adhere to different surfaces. These interactions come into picture when the distance between two molecules is less than 10 nm. These interactions can be attractive or repulsive. The extent of these forces depends on distance between the atoms, their polarizability and dielectric constant of the medium [92-93]. The force can be given by:

\[ W(D) \propto \frac{-A}{3D^3} \]  

(2.7)

Where \( W \) is van der Waals interaction, \( D \) is distance between molecules and \( A \) is Hamaker constant, given by:

\[
A = -\frac{3}{2} kT \left[ \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right] \left[ \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right]
\]  

(2.8)

Where \( \varepsilon_1 \) is dielectric constant of surface 1, \( \varepsilon_2 \) is dielectric constant of surface 2 and \( \varepsilon_3 \) is dielectric constant of the medium.

For an adhesive to be effective, it is important that it has both liquid like and solid like properties. Liquid like properties allow it to wet the bonding surface, thus allowing a very large area of contact. Solid like properties allow it to sustain a certain level of stress during de-bonding. This solid to liquid transition may occur via some stimuli, like change of temperature, solvent evaporation or some chemical reaction. However, such adhesives cannot be used in applications where continuous bonding and de-bonding is required. Pressure sensitive adhesives (PSA), based on viscoelastic materials, can stick to different surfaces without involving any change of temperature or solvent evaporation. Such adhesives could be used reversibly, but being viscoelastic they have some inherent
shortcomings [94-96]. Viscoelastic PSA has low modulus which puts a limit to maximum stress they can hold. Viscosity makes peeling a rate dependent quantity and at high rates, a lot of energy is dissipated which would be unfeasible for applications requiring rapid adhesion and peeling, e.g. for wall climbing robots. Being viscoelastic these materials show creep and their tacky nature makes them susceptible to contamination. The above challenges can be addressed by forming an elastic adhesive system.

To attain high area of intimate contact using an elastic system is challenging. The answer to this problem is found in foot of gecko lizard. Geckos use adhesive structure on their feet to climb vertical surfaces at high speeds. Microscopic studies revealed that the gecko foot is composed of thousands of microscopic hair called setae which further divide into hundreds of nanoscopic hair called spatula [97,98]. Figure 2.15 shows gecko foot on various levels. Figure 2.16A, 2.16B shows a comparison of how a liquid and a solid system can achieve large area of contact with the bonding surface.
Figure 2.15: Structure of a gecko foot. The above figure shows different levels of hierarchy found on gecko foot. (A) Optical image showing macroscopic structure of gecko feet. (B) Optical image showing lamella like structures (scansor) on toes. (C) SEM image showing each scansor is composed of thousands of microscopic hair called setae. (D) Setae further divide into nanoscopic hair called spatulas [98].

These hairs are formed of protein called keratin, which is a high modulus protein. When pressed against any surface these hair bend and conform to the surface, thus allowing very large area of intimate contact. Such high area of contact translates van der Waal’s interactions into high adhesive force. Diameter of hair depends on the weight of organism. It is seen that heavier animal have smaller foot hair diameter. Arzt, et. al. explained why smaller diameter hairs are required to sustain higher load using split contact mechanism [99]. The mechanism says that smaller diameter systems have larger
area of contact as compared to large diameter systems, thus net adhesive strength of smaller haired systems go up. Figure 2.16C shows split contact mechanism, which state how smaller diameter hairs can have higher area of contact with adhering surfaces as compared to thicker fibers. Inspired from structure found on gecko foot, many synthetic structures have been synthesized to mimic gecko like adhesion using polymeric pillars [100-102]. In some cases hierarchical structures [103] were also formed. The adhesion values of polymer based systems were much lower as compared to those of natural gecko. The main reason behind such behavior was higher diameter of polymer pillars. The other shortcoming of polymer pillars was that the structures would get destroyed due to low modulus of polymer used.

Yurdumakan, et. al. showed that CNT can be a potential candidate for developing gecko inspired adhesives owing to their small diameter and high modulus. In their experiment using AFM, they showed that a single CNT hair had two hundred times higher adhesion than a single gecko foot hair [104]. Following that discovery, a number of attempts have been carried out to achieve adhesion on a macroscopic scale. For such systems microscopic adhesion cannot be achieved on a macroscopic scale by just generating larger sample [105]. On a macroscopic scale, modulus of the backing material plays an important role in achieving high adhesion. Flexibility of the backing material not only allows larger area of contact, by conforming to macroscopic curvature of the bonding surface but also determine deformation of the hair. In the current work synthetic adhesives based on CNT were developed and it was shown that these systems have four times higher adhesion than natural gecko foot.
Figure 2.16: Split contact mechanism (A) A cartoon showing, conventional adhesive forming a high area of contact with two bonding surfaces by flowing and filling in the gaps (B) Cartoon showing mechanism of adhesion of elastic hair. The hair could bend and conform to the topology of the surface thus allowing very high area of contact with the bonding surface (C) Split contact mechanism, explains why a smaller diameter hair could have higher area of contact than a thicker fiber, thus leading to higher force of adhesion [99].

2.5 Electron Emission

Electron emission is a name given to the phenomenon where electrons leave the surface of metal and enter into vacuum. Electron emission may occur by various external stimuli like electric fields, high temperature or bombarding by high energy radiations [106]. The
energy difference between the vacuum potential, at which an electron just escapes from the metal surface and Fermi level in a metal, is known as the work function, usually denoted by $\Phi$. The work function is usually defined in electron-volts (eV) [107]. Thus, energy required by an electron to escape a surface is $E_f + \Phi$; where $E_f$ is the Fermi energy level. I would be discussing four methods of obtaining electron emission from the metal surface: (a) Thermionic emission, (b) Secondary emission, (c) Photo emission and (d) Field emission.

Thermionic emission: In this process the excess energy required for escaping the surface is derived from thermal kinetic energy. At temperatures $>900^\circ$C, thermal energy of sufficient electrons is large enough for escaping the surface. If the speed of electron, perpendicular to the surface of metal at given temperature is given by $v_x$ then, for emission to occur: 

$$\frac{1}{2}mv_x^2 > E_f + \Phi.$$  

Where $E_f$ is the Fermi energy level and $\Phi$ is the work-function of electron. The total current density ($J$) in this case is given by Richard-Dushman equation [108]:

$$J = AT^2\exp\left(-\frac{\Phi}{k_bT}\right) \quad (2.7)$$

Where:  

$$A = 4\pi e^2m k_b^2/h^3 \quad (2.8)$$

In the above equations, $J$ is the current density, $T$ is the temperature of emission, $\Phi$ is the work function, $k_b$ is Boltzmann’s constant, $e$ is charge on electron in eV, $m$ is mass of electron and $h$ is Plank’s constant. From the above equation we can see that the thermionic current is an exponential function of temperature. Electron emitter is known as cathode and the plate where electron is received is known as anode. Commonly used cathodes for thermionic emission are based on tungsten because of its high melting point.
However tungsten has a high work function (4.52 eV), therefore needs high temperature before it starts emitting electrons (2500K) [109].

Secondary emission: Secondary emission is the name given to electron emission from a metallic surface by bombarding with external electrons or other high energy particles. These high energy particles, when strike the metal surface, transfer their kinetic energy to the free electrons in metals. If the energy of striking particles is large enough, electrons in metals would be knocked off the metal. Secondary emission can give information about surface of metals. Auger and other electron spectroscopy techniques are based on secondary emission [110].

Photo Electric Emission: In this type of emission the additional energy come to the cathode by photons. When a beam of light strikes the surface of cathode the energy from photons is transferred from the photons to free electron within the cathode. If the energy from photons is greater than the metal work function the free electron will knock out from the cathode surface. The emitted electrons are called photo electrons. The amount of photo-electrons (photo-current) is proportional to the light intensity [111].

Field emission: In field emission, energy required for electron to escape the metal surface comes in the form an electric field. Electrons move in a direction opposite to electric field. Under high electric field, electrons may acquire kinetic energy large enough to overcome the surface potential and emit from the metal surface [112]. Field emission can be obtained at temperature much lower than required for thermionic emission and therefore it is also sometimes called as cold cathode emission. [113]. Low temperature in field emission makes the process attractive for applications where thermionic emission cannot be used, e.g. field emission displays. However for smooth
parallel metal plates it was seen that the electric field required to cause emission is of the order $10^3$ V/micron. However if the surface is made rough, such that electric field lines are more concentrated at a point, emission can occur at much lower voltages [115]. This phenomenon can be visualized from following figure:

![Electric field lines](image)

**Figure 2.17:** Electric field lines between cathode and anode. (A) Electric field lines between parallel plate anode and cathode. (B) Enhancement of electric field lines on needle like cathode. In case of pointed cathode, local electric field is much higher than average electric field.

In case of pointed cathodes the enhancement of electric field is quantified by a parameter called enhancement factor. This enhancement factor is denoted by $\beta$. For parallel plate configuration electric field intensity is given by:

$$E_s = \frac{V}{d}$$

(2.12)

Where $E_s$ is electric field intensity, $V$ is potential difference between cathode and anode and $d$ is the distance between cathode and anode. In case where surface is pointed, electric field intensity at point of emission is given by:

$$E_s = \beta \frac{V}{d}$$

(2.13)
Fowler and Nordheim derived the equation for emission current density under given electric field and it is known as Fowler-Nordheim equation for electron emission from cold metals [114]. The equation for parallel plate electrodes is given by:

\[ I = S \cdot a \cdot \frac{E_s^2}{\phi} \exp\left(-b \cdot \frac{\phi^{3/2}}{E_s}\right) \]  

(2.11)

Where:

- \( S \) = area of emitting surface
- \( E_s \) = uniform electric field on that surface
- \( a = 1.54 \times 10^{-6} \text{ AV}^{-2}\text{eV} \)
- \( b = 6.83 \times 10^7 \text{ eV}^{-3/2}\text{Vcm}^{-1} \)

For the case where there is an enhancement of electric field, Fowler-Nordheim equation for current density is given by:

\[ \frac{I}{V^2} = S \cdot a \cdot \frac{b^2}{\phi d^2} \exp\left(-b \cdot \frac{\phi^{3/2} d}{\beta V}\right) \]

(2.14)

If natural logarithm of equation 2.14 is taken, a straight line between \( \ln(I/V^2) \) and \( 1/V \) can be plotted. This is known as Fowler-Nordheim curve.

\[ \ln\left(\frac{I}{V^2}\right) = (-b \cdot \phi^{3/2} \frac{d}{\beta}) \frac{1}{V} + \ln\left(S \cdot a \frac{b^2}{\phi d^2}\right) \]

(2.15)

The slope of this line is: \( m = -b \phi^{3/2} d/\beta \). The value of slope can be used to determine enhancement factor. The intercept \( y_0 = \ln[aS\beta^{3/2}/(\phi d^2)] \) can be used to determine actual area of emission, \( S \).

Current-voltage (I-V) relation in a field emission is determined by slowly increasing the voltage and monitoring the current. The current would be zero up to value
of voltage called threshold voltage. At threshold voltage, electrons gain enough energy to escape the metal surface and sudden increase in current is observed. A typical I-V curve in cold emission is shown schematically in Figure 2.18.

![I-V characteristics of emission current. The above sketch shows typical I-V behavior of emission current. The current is zero up to threshold voltage. Above threshold voltage, current increases exponentially. The inset shows plot of ln \( (I/V^2) \) vs \( 1/V \). The slope of line is determined to evaluate enhancement factor. The inset shows Fowler-Nordheim curve.]

Higher enhancement factor is desirable to achieve electron emission at low threshold voltages. For this purpose pointed needle-like cathodes are desirable. With advancement in material science nanometer sized metal cathodes can be synthesized. However, if a large number of such needle-like cathodes are present in close proximity of
each other electric field of individual electrodes interfere with each other and net enhancement factor would go down. Such effect is shown by a sketch in Figure 2.19.

Figure 2.19: Screening effect. The above sketch shows how presence of large number of cathodes in close proximity to each other reduces net enhancement factor.

An example of electron emission from metal nanowires is shown in figure 2.20 [116]. Aligned tungsten nano wires with diameter of 10-50 nm were used in this case. It was observed that emission occurred at threshold voltage of 5V/μm with an enhancement factor of 38,256. The disadvantage of this process was that the tungsten nano-wires had poor alignment which led to lower current density.
Figure 2.20: Emission from tungsten nanowire [116]. The above figure shows electron emission from tungsten nanowires under electric field. The inset shows phosphorescence induced by electrons emitted by tungsten wire.

Other nano-material that has been extensively studied for field emission behavior is CNT. In 1995, Dr. Smalley’s group at Rice University showed emission from a single carbon nanotube [117]. The measurement was done by mounting a CNT on tungsten filament and bringing it close to another electrode, under vacuum. Figure 2.21 shows an image of experimental geometry that was employed to measure emission. It was observed that the emission from a single carbon nanotube started at much lower voltages than the corresponding metal wires of similar dimension (0.04V/μm). The hypothesis given was that CNT have atomically sharp wires dangling out of ends.
Following that discovery a significant research has been focused on realizing emission from CNT on macroscopic scale [118-125]. An example of emission from an array of CNT is shown in figure 2.22.
Figure 2.22: Emission from an array of CNT [118]. CNT used for the above experiment were 20 μm high. The total area of cathode was 1 mm$^2$ grid. Distance between anode and cathode was 1 cm. The experiment was done under 10$^{-6}$ torrs vacuum.

As compared to a single CNT, for an array of CNT many challenges are faced to achieve efficient electron emission. Some of these challenges include, pull-off of CNT under high electric field, uneven height of array and screening effect. Overcoming above challenges is important for effective use of CNT based field emitters in applications like displays. In the current work CNT-polymer composite structures were developed to address some of these challenges.
CHAPTER III

VERTICALLY ALIGNED CARBON-NANOTUBE COATINGS

3.1 Introduction
Vertically aligned CNT are very important for many applications, like in microelectronics, optics and for dry adhesives. They offer unique structural properties due to small dimension of CNT. In the current work aligned carbon nanotube structures were synthesized using chemical vapor deposition process. These aligned CNT were then transferred in polymer matrices to form a carbon nanotube-polymer composite structure. This composite structure offered many unique advantages over existing carbon nanotube structures due to its high mechanical stability and superhydrophobic behavior. It was shown that this composite system could be used for making self-cleaning adhesives and flexible electron emission devices [126-130].

In the current Chapter synthesis of CNT using chemical vapor deposition process would be discussed. Various carbon nanotube structures would be discussed in relation to carbon source used. Process for forming carbon nanotube-polymer composite structure would be described. Section 3-4 would talk about three main applications developed based on such structures, (a) Superhydrophobic coatings, (b) Self-cleaning adhesives, and (c) Electron emission devices.
3.2 Carbon-Nanotube synthesis

CNT were grown by chemical vapor deposition process (CVD). Setup for CVD included a three zone heating furnace with a 60” long fused quartz tube inserted in it as shown in Figure 3.1. The three-zone heating allowed having a uniform temperature over a long region. This allowed uniform carbon nanotube growth over a large area. Temperature profiling of the furnace was done at 660°C. A J type thermocouple probe with 8’ long stainless steel 304 armored cable was used for temperature profiling. The thermocouple was inserted in the furnace at different distances and temperature was measured. The temperature profile of the furnace is shown in Figure 3.2, it can be seen that a uniform temperature can be obtained over a region of 20”.

Figure 3.1: Image of CNT furnace. The above image shows an optical image of three zone furnace used for synthesis of CNTs using chemical vapor deposition process.
Figure 3.2: Temperature profile of tube furnace. The above graph shows temperature profile in the three zone furnace with all the zone temperatures set at 660ºC (the above data was collected by Michael C. Heiber). It could be seen that at edges the temperature falls rapidly because the edges are in contact with atmospheric conditions. The region in center of the furnace had a uniform temperature over the length of 20”. This zone of uniform temperature would go down with increasing temperature and increase with increasing temperature. Temperature profile was measured with the ends of quartz tube open. This causes excess contact with atmospheric air. In actualy operation the ends are closed. Thus the active zone would be longer in actual operation.

The furnace with all its components is shown by sketch in Figure 3.3. The quartz tube was connected to argon, hydrogen and acetylene cylinders using individual flow meters. A syringe pump is used to pump carbon source and catalyst in a sublimation chamber where metal catalyst-carbon source mixture is evaporated. This gaseous mixture is then carried in the furnace via flow of argon-hydrogen mixture. The exiting end of the furnace is connected to a water bubbler, which would help in removal of excess gases. Finally the gases enter the exhaust system.
CVD process used for the current work is called floating catalyst method. It derives its name from the fact that the catalyst is not deposited on the substrate as with conventional CVD process but is mixed with the carbon source and introduced in the furnace in vapor form. The advantage of this system is that it allows growing of CNT on complex shapes, which is not possible using catalyst deposition process. For the current work micropatterned vertically aligned CNT grown via catalyst deposition process were also used. These nanotubes were prepared in Dr. Ajayan’s lab at Rice University. The process of catalyst deposition allows use of photolithography to pattern the substrate. This allowed us to create nanotubes in various square patterns for synthesis of carbon nanotube based dry adhesives.
Catalyst used for floating catalyst method was ferrocene (dicyclopentadienyl iron). Ferrocene is an organometallic compound with two pentadienyl rings joined at center to a iron atom using coordination bonds. Its chemical formula is \( \text{Fe(C}_5\text{H}_5\text{)}_2 \). Ferrocene was used as the catalyst because it is the most stable of mettalocene catalysts. Iron has 10 vacant sites in its d-orbitals, in ferrocene molecule each pentadienyl donates five electrons to iron, thus giving iron noble gas configuration. This makes handling of ferrocene much easier. The two pentadienyl groups also help in dissolution of ferrocene in various organic solvents like xylene, toluene, chloroform and ethanol. This makes this very a useful catalyst compound, since many of these solvents also act as carbon source for carbon nanotube growth. The chemical structure of ferrocene is shown below:

![Chemical structure of ferrocene](image)

Figure 3.4: Chemical structure of ferrocene.

For the current work xylene and ethanol were used as carbon source. Silicon wafer with a layer of silicon dioxide on the surface was used as the substrate for growth of aligned nanotubes. Silicon substrates used for the growth have very smooth surface. This is important to achieve aligned nanotube film with uniform height. Other substrates
such as fused quartz, aluminum and stainless steel were also used for growth of CNT. Before the growth process the substrate need to be cleaned thoroughly. Substrates with impurities on the surface would lead to uneven and ineffective growth. To clean the substrates, they were sonicated in soap solution for 30 minutes. They were then washed with de-ionized water thoroughly. The samples were then dried using pressurized nitrogen. The dried substrates were then treated in oxygen plasma for 5-7 minutes. Treatment in oxygen plasma oxidizes any remaining organic molecule on the surface of substrate.

The cleaned substrates of desired shape and size were then placed in furnace. The furnace was heated to desired temperature in argon hydrogen environment. For silicon and quartz this temperature ranged from 700°C to 800°C. In case of aluminum substrates this temperature was from 600°C to 640°C. On reaching the desired temperature carbon source and catalyst mixture was injected in the system. CNT were grown for twenty minutes to one hour.

CNT growth process conditions were optimized so that large areas (25 cm²) of uniform carbon nanotube array of lengths greater than 1 mm could be grown. It was seen that these structures had high structural integrity and can be peeled off the substrate to form a free standing film. Figure 3.5 shows an example of large area of vertically aligned carbon nanotube structure grown using floating catalyst method. Electron microscopy was used for characterization of carbon nanotube structure. Figure 3.6 shows scanning electron microscope (SEM) image of aligned carbon nanotube structure. From the Figure it can be seen that the nanotubes grow perpendicular to the surface. The top surface of carbon nanotube array is shown in the inset.
Figure 3.5: Vertically aligned CNTs grown on silicon substrate. The above Figure shows CNT grown on SiO₂ substrate at 800°C with carbon source injected for 1 hour at 0.11ml/min. (A) Shows optical image of the silicon wafer with CNT on it. The size of substrate was 5 cm X 5cm. (B) Shows a 1 cm X 1 cm piece of carbon nanotube peeled off from the mat.
Figure 3.6: SEM image of CNT array. The above image shows scanning electron micrograph image of CNT grown on SiO₂ substrate. The length of the nanotube array was around 800 microns. The inset shows top view of these nanotubes.

To see the structure of individual carbon nanotube, transmission electron microscope (TEM) images were taken. The TEM images confirm that the structures grown are hollow cylinders; therefore these are CNT and not carbon nanofibers. The transmission electron micrograph of grown CNT is shown in Figure 3.7.
Raman spectroscopy was done on these carbon nanotube structure. There are four major peaks in raman spectrum of CNT. G-line, D-line, G’ and radial breathing modes (RBM). G-line is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of the carbon atoms. Peak of G-mode generally lies around $1580 \text{ cm}^{-1}$ for carbon-nanotubes. D and G’ bands arise from second order Raman-scattering. D-band signifies defects in graphitic structure. Higher intensity of D-mode would mean more defects in carbon nanotube structure. D-band Lower intensity would mean long range order. Radial breathing modes (RBM) are characteristics of diameter of nanotubes. RBM modes are very sensitive to diameter of single walled nanotubes and double walled
nanotubes. Raman analysis of CNT grown by above process had a sharp G-band and a small D-band [131-132]. This signifies that the array had uniform diameter CNT with long range order. Raman spectrum is shown in Figure 3.8.

![Raman spectrum of CNT array](image)

Figure 3.8: Raman spectrum of CNT array. The above graph shows Raman spectrum of aligned CNT arrays grown on silicon substrate using xylene as chemical source. Raman spectrum showed that the CNT had long range order. (The Raman spectrum was taken with the help of Andrew Malkowsky in Dr. Alexei Sokolov’s laboratory).

In CVD growth, surface of the substrate is very critical for growth of CNT. In case where there are impurities like oil on the substrate, de-wetting takes place and there might be various kinds of defects on the surface. These defects may include regions with no CNT growth. Figure 3.9 shows SEM image of silicon substrate with non-uniform CNT growth.
Figure 3.9: Defects in CNT film. The above SEM image shows defects in the CNT film grown on silicon dioxide surface. This is due to improper cleaning of substrate. It could be seen that these are islands as big as 100 microns, where CNT have not grown.

Choosing right carbon source is very important for controlling growth of CNT. For the above shown structures, xylene was used as carbon source. It was observed that when ethanol is used as carbon source the growth rate was much less than when xylene was used as carbon source. This could be explained based on slight oxidising nature of ethanol. Xylene-ethanol mixtures were used to study this phenomenon. When a xylene:ethanol::90:10 mixture was used as carbon source, the resulting carbon nanotube array grown was optically darker than those grown using xylene process. TEM and
Raman analysis were done on these structures to visualise the difference in the spectrum. From TEM images it was observed that the CNT grown using xylene-ethanol mixture had thinner walls compared to those grown using xylene. Additionally, there was a larger variation in the length of the CNT grown using the xylene-ethanol mixture. The height of carbon nanotube array grown using xylene-ethanol mixture was 200 microns but it was observed under TEM analysis that some of the CNT were only 100 nm in length. These small tubes were not broken fragments of longer CNT tubes because both ends of the tubes were capped. Such mixture of long and short CNT in the array can yield low density carbon nanotube array.

Figure 3.10: TEM image of CNT grown using a mixture of xylene and ethanol. It was observed that CNT had thinner walls. Many small CNT were also observed. It can be observed that these small nanotubes have both ends closed.
Percent area coverage was calculated by image analysis of carbon nanotube image. The pixels of image were converted into numbers based on intensity of that pixel, using matlab. From the above SEM image it can be seen that the CNT which are on surface have higher intensity pixels as compared to background. The intensity of pixels was normalized, such that brightest pixel has intensity 1.0 and the darkest one 0. Distribution of such pixels was then plotted. Surface coverage of CNT was calculated by finding the ratio of area covered by pixels above 0.8 to the total surface area. The value
0.8 was chosen empirically, by comparing different areas of the sample. It was seen that percent coverage for intensity between 0.9 and 1.0 is 3%. For intensity between 0.8 and 1.0 is 17%. This means that the whole structure is highly porous. Such high porosity is important for wetting properties of the structure.

Figure 3.12: Surface coverage of CNT array using intensity analysis. The above graph shows normalised intensity of a SEM image of carbon nanotube structure versus total number of pixels. The brighter pixels represent CNT on surface. Medium intensity pixels represent lower layers of CNT and dark pixels represent blank spaces.

For development of dry adhesives micropatterned CNT were used. These nanotube structures were grown at Rice University by Dr. Lijie Ci. Photolithography was used to deposit catalyst in the desired pattern. For current work these patterns were square patterns with edge length ranging from 50 microns to 500 microns. CNT were
then grown using CVD process with acetylene as carbon source. Figure 3.13 shows one such example of patterned carbon nanotube.

Figure 3.13: SEM image of patterned CNT. The pattern is square pattern with edge 500 microns (these nanotubes were grown at Rice University, in Prof. P. M. Ajayan’s laboratory).
3.3 Carbon-Nanotube polymer composite system

Flexible and rigid films of vertically aligned CNT were formed by forming a composite structure of aligned nanotubes in polymer. This composite structure gave stability to carbon nanotube array and allowed coating of carbon nanotube films on different surfaces using polymer matrix as interlayer. Such structures allowed formation of conductive superhydrophobic coatings, self cleaning adhesives and flexible electron emitting devices.

Figure 3.14: High resolution SEM image of patterned CNT.
The transfer process was such that carbon nanotube array is partially embedded in the polymer. The interlayer was chosen such that it is viscous liquid to start with. This viscous liquid was coated on different surfaces using techniques like spin coating and casting. The thickness of this film was regulated such that it was less than the length of CNT but large enough to account for irregularities in height of the carbon nanotube array. CNT grown on silicon wafer were then inverted on this tacky material and were pressed gently to make uniform contact. This was followed by solidification of the tacky material by cross-linking, polymerization, temperature change or solvent evaporation. Once the material solidified, the Si wafer was peeled off and the CNT array was transferred onto the substrate. The outline of this process is shown in Figure 3.15. The polymer used must have suitable viscosity, such that the polymer network has certain tackiness associated with it. This tackiness allows ends of CNT to penetrate in the network. However, the viscosity should be high enough so that the polymer does not cover the CNT structure.
Figure 3.15: CNT transfer process. The above sketch shows a procedure used to transfer aligned CNT on different surfaces (polymers, glass and metals). A thin layer of tacky polymer is coated in the base on which carbon nanotube are to be transferred. The thickness of the glue should be less than the length of CNT and the viscosity should be high enough so that CNT do not get coated with the glue. The silicon wafer with a carbon nanotube array grown on it is then pressed on to the glue. The glue is allowed to solidify. The silicon wafer is removed in the final step, to yield a carbon nanotube array embedded on the base.

In CVD process carbon nanotube array grown may have surface unevenness. The end of array in contact with the silicon wafer is more uniform. When transferring CNT using the above-described process, edge in contact with the silicon wafer face upwards, thus enabling formation of a uniform structure. This phenomenon is shown using a sketch in Figure 3.16.
Figure 3.16: CNT transferred in the polymeric matrix. The above sketch shows how the transferring of CNT in the polymeric matrix helps to form a more uniform upper surface. As grown CNT may not be absolutely uniform at the surface. Some areas may have longer nanotubes than other areas. The other end of nanotubes, which faces Si wafer have much higher surface uniformity. CNT maybe transferred onto a polymeric matrix in a way that the uniform surface is exposed on the top. (A) As-grown CNT (CNT) on Si wafer. (B) As-grown wafer inverted onto a polymeric matrix with adhesive layer on top of it. (C) Si wafer removed and CNT transferred on polymer matrix with smooth surface on the top.

Transferring CNT in polymer matrices using above described process is highly versatile. It allows choosing different recipes to be used for different applications. Some of these recipes are discussed below:

1. Using a pre-polymer: For example poly (dimethylsiloxane) and crosslinking the matrix after embedding the tubes in the matrix.

2. Using a monomer like cyanoacrylate and embedding the tubes in the polymer film and letting it polymerize to form solid film.

3. Dissolving the polymer in a solvent to form viscous solution. Coating the solution on a rigid substrate. Embedding the tubes in the wet film and letting the solvent evaporate (for example, poly (methyl-methaacrylate) in toluene).

4. Chemical reaction between two components to yield a solid substrate (for example, epoxy resins).
5. Softening of a thermo plastic by heating it above its glass transition temperature and embedding nanotubes in the softened polymer matrix followed by cooling of system.

Using the above methods, aligned carbon nanotube structures were transferred on a variety of surfaces (glass, metals and rubber). We showed that very small areas (0.5mm x 0.5mm) to large areas (2 cm x 2 cm) of carbon nanotube arrays were transferred using this technique. The following optical image shows aligned nanotubes transferred onto a glass slide using poly(cyanoacrylate).

Figure 3.17: CNT embedded in poly(cyanoacrylate) on a glass slide. The nanotube structure remained intact after transfer process. Length of exposed end of CNT can be controlled by controlling the thickness of polymer interlayer.
Nanotubes were transferred onto flexible polymers like poly(dimethyl siloxane). The following image shows a patterned carbon nanotube transferred in poly(dimethyl siloxane).

![Image of CNT embedded in PDMS matrix using PDMS as interlayer.](image)

Figure 3.18: CNT embedded in PDMS matrix using PDMS as interlayer. Optical image of 250 micron pattern size CNT embedded in PDMS matrix using PDMS as interlayer. This process yielded flexible film with aligned nanotube brushes on one end.

Poly(dimethyl siloxane) has a very low surface energy and tended to coat any surface it comes in contact with. Poly(dimethyl siloxane) was partially cured before transferring CNT in it. EDAX spectrum was taken to confirm that the surface of CNT do not have any siloxane polymer. The following spectra show that there is no silicon peak. Therefore we can conclude that silicone polymer is not contaminating the nanotubes.
Figure 3.19: EDAX spectra of CNT embedded in PDMS. For a pure PDMS film, Si peak can be seen. Absence of such peak signifies that PDMS is not contaminating carbon nanotube structure.

Using the above process aligned nanotube structures were transferred in conductive matrices. This is very important for use of aligned structures in electronics. Conductive silver epoxy was used to transfer CNT onto different surfaces. Silver epoxy forms a thin uniform layer on the substrate and forms a conductive backing for CNT.
3.4 Wetting

Vertically aligned nanotubes have a very porous structure, thus they can show very high water contact angle. It has been reported in literature that even though aligned nanotubes show a high water contact angle, but the structure collapses under capillary action of water [133]. In Figure 3.21 this process is shown schematically.
Figure 3.21: Sketch showing wetting behavior of aligned nanotubes, (A) Sketch showing that aligned nanotube has highly porous structure. The air trapped in between the pores helps them attain high contact angle. (B) Shows a water droplet sitting on CNT. Individual CNT are slightly hydrophilic. The whole structure is superhydrophobic because of air trapped in between the pillars. (C) Shows that capillary force acts on bringing the nanotubes together. This causes collapse of nanotube structure.

It was seen in previous work that when water droplets are placed on aligned nanotube network, the capillary forces tend to pull the hairs together. This destroys the structure of aligned nanotube and the system no longer shows high contact angle. By partially embedding CNT in a polymer matrix, the whole structure gets more stable. It
was seen that water formed contact angle of greater than 150° on such structures. The following Figure shows an example of wetting properties of carbon nanotube structures embedded in PDMS matrix.

Figure 3.22: Water droplets on patterned CNT embedded in polymer matrix.

Figure 3.23: Carbon nanotube-polymer composite structure. The above sketch shows different layers of CNT-polymer composite structure.
For applications such as self-cleaning, it is important that the material not only have high water contact angle but also low contact angle hysteresis. This low hysteresis allows water to roll down the surface easily. It was seen that on carbon nanotube-polymer composite structure water would roll down at very low tilt angles. High speed camera was used to visualize this effect. A 10 micro-liter droplet was put on carbon nanotube structures kept at an angle. The following image shows high speed camera images of water rolling down carbon nanotube surface.

Figure 3.24: Water droplet rolling down CNT array. The above figure shows high speed camera image of water droplet rolling down the carbon nanotube structure.
3.5 Adhesion

The current section discusses adhesive properties of CNT based fibrillar adhesives. The mechanism of adhesion of such systems is discussed in detail in Chapter II. It was shown by Yurdumakan, et. al. that a single carbon nanotube has 200 times higher adhesion than gecko setae. Translating this adhesion on a larger scale was challenging because macroscopic areas are not truly parallel. A flexible backing was required to attain efficient adhesion on macroscopic scale. CNT arrays transferred in polymer matrix were used for this purpose. This geometry of aligned nanotubes embedded in polymer matrix would be referred to as gecko tape. The flexible matrix of gecko tape allowed taking macroscopic contours. Individual CNT could bend and conform, to form intimate contact on nanometer scale. Therefore by using gecko tape we were able to attain intimate contact over large areas. To test the adhesion, small areas of flexible gecko tapes were pressed against a smooth mica sheet using a cylindrical roller by applying a pressure of 25–50 N/cm². This preload was important to deform the gecko tape and allow the carbon nanotube structures to achieve good contact between the tape and the substrate. The actual shear measurements were done under no external normal load. Gecko tape was then pulled parallel to the surface under constant force. The values for adhesion forces are reported in force per unit contact area. The geometry used for measuring adhesion is shown in Figure 3.25.
Figure 3.25: Setup for shear force measurement. The above sketch shows geometry used for measuring shear adhesion of gecko tape on different surfaces. The force was applied by hanging dead weights.

The gecko tape adhered to different surfaces, with a force comparable to that seen for natural gecko (10 N/cm²). To verify that the interactive forces between gecko tape and substrate were vdW, adhesion of gecko tape on surfaces with different surface energies was tested. Figure 3.26 shows adhesion force of gecko tape on four such surfaces. Glass and mica have high surface energy and are highly hydrophilic surfaces. Poly (methylmethacrylate) is slightly hydrophilic and side chain acrylate polymer (poly (n-butylacrylate) is highly hydrophobic. It was observed that adhesion strength of gecko tape on different surfaces is similar. This signifies that the adhesion is not specific to chemistry or hydrophilicity of the material. This suggests that the adhesive forces are due to vdW interactions.
Figure 3.26: Adhesion of gecko tape with various surfaces. The sample size in all these cases was 4mm x 4mm. Sample was stuck onto different substrates by applying a preload. The preload was then removed and gecko tape pulled parallel to substrate using constant force.

However, the adhesion force of the un-patterned synthetic gecko tape, instead of increasing linearly, decreases with increase in contact area and it is not possible to support larger forces by just increasing the contact area. This is a disadvantage because the weight supported by the gecko tape cannot be increased just by increasing the contact area.
Figure 3.27: Shear force per unit area vs area. It could be seen from the above histogram that the amount of force sustained per unit area went down as the total area of gecko tape was increased.

Such behavior can be understood by looking at the structure of gecko foot. Gecko foot is not completely covered with hair but has an intricate hierarchical structure. Such hierarchical structure is important to attain high shear force on large areas. The hierarchical structure provides resistance to the propagation of cracks, which is very important in increasing the toughness of the materials. Kendall has shown that the peeling strength of tapes with patches of different stiffness or thickness can be much higher than the tapes with uniform thickness and stiffness [134]. Chaudhury and coworkers have used 100-200 µm patches on poly(dimethylsiloxane) (PDMS) sheets to increase the peeling force by a factor 10-20 in comparison to a unpatterned PDMS sheet.
The mechanism in all these cases is to stop, deviate, and reinitiate the crack propagation in comparison to materials with uniform properties (also referred to as the Cook-Gordon mechanism) [135]. Based on Cook-Gordon mechanism and Manoj Chaudhary’s calculations, if a patterned nanotube sample is prepared it will show much higher adhesive force as compared to un-patterned sample. Micropatterned vertically aligned CNT were used to replicate the multi-scale structure of setae and spatulas. It was seen that not only nanometer-length scales of spatulas (individual CNT) but also micrometer-length scales of setae (patterns of CNT) are important to support large shear forces. Using patterned surfaces with features of 50 and 500 µm wide, a factor of four to seven times higher shear force was obtained as compared with the un-patterned surfaces of similar area. The shear force supported by the 100 µm to 500 µm patches is 3.7 N, which is two to three times higher than the natural gecko. The advantages of patterns became less prominent on reducing the patch size to 50 µm (and 300 µm in height) because a decrease in the ratio of the width to its height makes setae mechanically weak. When smaller height of the 50 µm setae (200 µm), were used, it was seen that the shear force is 5.8 N, a factor of four times higher than the natural gecko. Thus, not only pattern size but length of fibers is important to attain high adhesion on large scale.
3.6 Self cleaning

Carbon nanotube based synthetic gecko tapes adhere to different surfaces using van der Waal’s forces. These are non tacky substances which adhere only by application of preload. Therefore dust particles don’t stick to them, as they would to a viscoelastic tape. It was observed that the dust particles could be removed from gecko tape by application of small vibrations, by blowing air or by touching with a surface with high surface energy. This behavior could be explained by contact cleaning mechanics as seen in gecko feet. According to this theory, if a particle is in contact with two surfaces, it will transfer on surface with higher surface energy. Once soiled, geckos can clean their feet by just walking. Geckos remove their foot from ground by peeling their toes at an angle. Thus dust particles are removed from their feet. To test this behavior on synthetic gecko tape, silicon particles of sizes ranging from 1 to 100 µm in size were used to soil the surface of
gecko tape. The silica particles were used in these experiments to represent dust. The soiled gecko tape was then touched on mica substrate a few times. It was seen that dust particles would transfer on mica substrate. This behavior is depicted in Figure 3.29.

Figure 3.29: Self cleaning behavior of synthetic gecko tape. (A) Optical image of as grown carbon nanotube structure. (B) Structure soiled with silica particles. (C) Carbon nanotube surface cleaned by touching to mica substrate. (D) Surface of mica after dust particles transferred on it.

The dust particles can also be removed by blowing air on the surface of CNT. Another mechanism of self cleaning seen in nature is by making a surface superhydrophobic. This is also known as lotus effect. Optimized structures of synthetic gecko tapes show superhydrophobic behavior. Self-cleaning ability of gecko tapes using
water was tested. A droplet of water was allowed to roll off the surface. It was seen that water droplet rolls off carrying dust particles with it.

Figure 3.30: Optical image of water droplet sitting on gecko tape. The gecko tape demonstrated self cleaning behavior.
Figure 3.31: Self cleaning ability of CNT array. (A) Optical microscope image of patterned carbon nanotube structures soiled using silica particles. (B) Structure cleaned via rolling water droplet on the surface.
Therefore, gecko tapes can show self-cleaning abilities by both vibrations and using water. It was seen that these tapes recovered back their adhesiveness after self cleaning. It was seen that the tape retained back 80% adhesion strength for self cleaning by vibrations and 60% cleaning strength for self-cleaning by water. The number is slightly lower for cleaning by water because water caused formation of cracks in nanotube structure. The following histogram shows adhesion values for clean and self cleaned sample.
3.7 Field emission

In Chapter 2 electron emitting properties of CNT were discussed. A single CNT emit electron at low threshold voltages however many challenges are faced in achieving efficient emission at macroscopic scale. Some of these challenges are:

1. Non-uniform CNT matrix: Longer CNT would emit electrons at lower threshold voltage. Therefore at a given voltage only a few CNT may be emitting electrons. This leads to lower current density.

2. Pull-out of CNT: At high electric fields, it was observed that some CNT may get pulled out of array. This leads to formation of resistive contact between cathode

Figure 3.33: Adhesion of self-cleaned CNT array. The above histogram shows data for shear measurements of control, sample dusted and cleaned by applying vibrations or with water (the above measurements were done with the help of Liehui Ge).
and anode. This might lead to misleading current-voltage (I-V) curve and short-circuiting.

3. Screening effect: Due to proximity of neighboring CNTs electron emission from an array of CNT occurs at much higher voltages as compared to single CNT. It has been shown experimentally that screening effect can be reduced by using high aspect ratio aligned CNTs separated by distance equivalent to their height. However such structures can be generated only by using anodized aluminum oxide (AAO) templates. The disadvantage in using (AAO) templates is that small diameter CNT (< 10 nm) with well defined structure are difficult to grow in AAO templates. The second mechanism proposed to reduce the screening effect is by incorporating a dielectric material (like polymer) in between CNTs.

In the current work partially embedded CNT in polymer matrix (gecko tape) were used to create electron emission devices. Such geometry would help in overcoming above discussed challenges. CNT embedded in polymer matrix are very stable. The transfer process is such that it would reduce the surface unevenness of CNT array as shown in Figure 3.34. Presence of dielectric in between CNT could help in reducing screening effect and help in attaining emission at lower threshold voltages.
Figure 3.34: CNT-polymer structure for reducing screening effect. The above cartoon shows how transferring CNT on a polymeric substrate also allows us to incorporate a suitable dielectric material in between tubes without covering the tips of nanotubes.

Figure 3.35: CNT pull-off under strong electric fields. The above cartoon shows how CNT may get pulled off towards anode under high electric fields. This is a highly undesirable effect because it may cause short circuiting of the whole assembly.

Using the above process the whole geometry could be made flexible or rigid depending on desired application. As a specific case, poly (cyanoacrylate) films on glass were used to create rigid devices and poly (dimethylsiloxane) (PDMS) elastomer used to create flexible devices. The testing geometry was formed using ITO glass as anode and carbon nanotube structure as cathode.
Potential difference was applied across the electrodes. Current passing through the circuit was monitored using an ammeter in series. Anode and cathode were separated by a distance of order of $10^{-5}$ m. A micrometer driven jig was used for this purpose. The jig had lower portion fixed and connected to an electrical pin. The top portion (anode) could move up and down using the micrometer. The following images show design of setups used to measure field emission values:
Figure 3.37: Instrument used for measuring electron emission of CNT. The above image shows a micrometer driven instrument used for measuring electron emission behavior of CNT.

Emission behavior from CNT in atmospheric conditions was tested. The sample was prepared using poly(dimethysiloxane) as interlayer with aluminum backing. Before collection of data the sample is conditioned by applying high voltage. This is important to burn off any longer strands of CNT. Applying high voltage may also open the end of CNT and increase efficiency of emission. Figure 3.38 shows an example of conditioning of CNT array. The current increases linearly with applied voltage till a threshold value is reached. At certain voltage the CNT strand would get burned off and current intensity drop to zero.
The first run not only burns off the longer CNT but it also conditions the array. Due to electric field CNT get straightened. This increases the efficiency of emission. It was seen that in air, emission current density goes down with each consecutive run. Current density increases after the conditioning but it decreases continually after that.
Figure 3.39: Emission current for ten successive runs in air. The above histogram shows how the current drops with each successive run in air.

From the above graph it can be seen that the current intensity increases with the number of runs and then start decreasing. The initial increase in current intensity is due to conditioning of sample. The subsequent fall in intensity may be caused by oxidation. To reduce the oxidation of nanotubes electron emission behavior were tested in vacuum. Low vacuum chamber and high vacuum chambers for electrical measurements were built. The chamber had electrical throughputs, which allowed connection of anode and cathode inside vacuum chamber to voltage source and multimeter outside the chamber. The following image shows low vacuum setup, built for field emission measurements:
Figure 3.40: Instrumentation for measuring electron emission. The vacuum chamber has electrical throughputs. The throughputs could be connected to a sourcemeter outside vacuum, chamber. The data is then collected on a computer using RS-232 port.

It was seen that at vacuum of the order $10^{-3}$, the nanotubes would still get oxidized. At high emission current, visible sparks could be seen in the chamber. A high vacuum chamber was build to study the emission under high vacuum. The chamber consisted of a turbo pump, connected to a vacuum chamber. The chamber was fitted with vacuum gauge, an electrical throughput door and a high vacuum see through gate. The samples were placed in the chamber and connected to the electrical throughputs, which were then connected to Keithley 2400 sourcemeter. The vacuum chamber is shown in following Figures:
Figure 3.41: Ultra high vacuum chamber for emission measurement.
Figure 3.42: Measurement geometry in ultra high vacuum chamber. The above figure shows an optical image showing how the sample is placed inside the vacuum chamber.

Figure 3.43: Geometry of anode and cathode. The above optical image shows the geometry of anode and cathode.
The vacuum in high vacuum chamber was of the order of $10^{-6}$ mbars. At this temperature stable current behavior was seen. It was seen that the current behavior was more uniform at high vacuum. It was observed that in high vacuum, with currents as high as 300 $\mu$A the tubes were not getting destroyed. This was confirmed by repeated I-V measurements. It was seen that for 10 consecutive runs, current at 150V came out to be within 5%.

Figure 3.44 I-V curve of CNT transferred on a scotch tape. The measurement was done at $10^{-6}$ mbars.

From the above I-V curve it can be seen that emission from carbon nanotube array started at 40V. The distance between cathode and anode was 100 microns. Therefore
flexible electron emission devices formed using CNT start emitting electron at < 0.5 V/µm. Enhancement factor was calculated using Fowler-Nordheim curve. The enhancement factor of $10^4$ was observed.

Figure 3.45: Fowler-Nordheim curve for emission from CNT. From the above curve it can be determined that the structure showed an enhancement factor of $10^4$.

The system showed consistent threshold voltage over large number of runs. Such behavior is important for building devices based on flexible electron emitters. The efficacy of the system was tested by applying pulsed voltage. An example of pulsed I-V behavior is shown in Figure 3.46. The distance between electrodes was kept so that threshold voltage was around 100V. Repeated pulses of 50V, 100V, 150V and 200V
were applied. It was observed that there was no current at 50V and 100V. A consistent current of 250 μA was attained at 200V.

Figure 3.46: I-V characteristics by applying pulsed voltage. The above graph shows I-V characteristics of flexible field emission device by applying pulsed voltage.
To summarize, we synthesized flexible electron emission devices with high efficiency by embedding CNT array in polymer matrix. The current density achieved is higher than that reported in literature for flexible filed emission devices formed by CNT polymer composites [137-138]. In the previous processes, CNT matrix was completely embedded in polymer matrix which caused lower efficiencies. In the current work the CNT-polymer structure were developed such that aligned CNT array are partially entrapped in polymer matrix. The electron emitting devices based on gecko tape had low threshold voltage of $<0.5\text{V/μm}$. The current densities observed were of the order of $1\text{mA/cm}^2$. The efficiency could further be enhanced by using a micropatterned CNT structure and suitable dielectric material. Micro-patterning nanotubes would help in
achieving higher current densities over patterned nanotubes. Patterning increases number of edges on carbon nanotube films. Having higher number of edges would increase emission density from the edges.

Electron emission behavior was also tested for CNT grown directly on aluminum substrate. Figure 3.48 shows emission behavior of CNT grown on aluminum substrate.

![Graph showing emission from CNTs grown on Aluminum stub](image)

Figure 3.48: Emission from CNT grown directly on Aluminum stub. The above graph shows emission from CNT grown directly on Aluminum stub. Forming electron emission devices directly on aluminum substrates would open up possibilities of forming large area field emission devices on an inexpensive conductive substrate.
CHAPTER IV
NON-ALIGNED CARBON-NANOTUBE COATINGS

4.1 Introduction

In the previous section it was shown that vertically aligned CNT can be rendered superhydrophobic by partially trapping them in polymeric matrix. Yet, for applications involving high hydrostatic pressure on the structures aligned nanotubes fail. The solution to that problem lies in creating mesh like structures. Such structures have a higher stability as compared to aligned structures. Inspired from a need to create stable superhydrophobic structures, mesh like carbon nanotube coatings were formed on stainless steel (SS) surface.

In the current Chapter synthesis of these mesh like carbon nanotube coatings on SS is discussed. It was shown that these coatings have very high hydrostatic stability and can maintain their superhydrophobicity even after exposure extreme thermal stresses. Being composed of CNT, these coatings have high thermal and electrical conductivity. The second section of the Chapter describes a process developed to reinforce these coatings using polymers, without significantly losing the conductivity and superhydrophobicity. The above properties make these coatings suitable for applications for which existing superhydrophobic coatings cannot be used. The last section of the
Chapter discusses the test procedures developed to test these coatings for their floatation behavior, anti-ice coatings and for heat transfer furnaces.

4.2 Carbon-Nanotube synthesis

Non aligned CNT grown on Stainless steel 304 (SS) are discussed in this section. CNT were grown on SS using a chemical vapor deposition furnace as described in Chapter 3. In case of SS, extra surface treatment is required prior to carbon nanotube growth. SS has chromium oxide layer on the surface. It has been shown that this oxide layer inhibits growth of carbon nanotube [139]. The oxide layers were etched away by dipping SS substrates in 9N Sulfuric acid, at 80 °C, for 10 minutes. This was followed by washing the substrate with de-ionized water and drying using compressed nitrogen. Ferrocene:xylene ::1gm:100ml mixture was used as carbon source and catalyst. The CNT were grown at 750°C in argon-hydrogen atmosphere.

CNT structures obtained on SS substrate using this process had mesh like geometry. SEM image of the structure is shown in Figure 4.1. The structure could be visualizes as a stack of multiple layers with holes in them. Such structures are shown via a sketch in Figure 4.2.
Figure 4.1: SEM image of non aligned CNT. The above SEM image shows CNT structure as grown on SS. The structure is formed of multiple layers of mesh like carbon nanotube structures. This multiple layer gives high stability to the whole geometry.

Unlike aligned nanotube geometry, the mesh like structure have CNT interwoven amongst each other. This gives them high stability against capillary forces. The reason for growth of non-aligned CNT on SS substrate as compared to aligned growth on Si wafer can be attributed to highly rough surface of the substrate. CNT are known to grow perpendicular to the surface as described in Chapter 3. Silicon wafers used to grow aligned nanotube geometry have a very smooth surface as compared to stainless steel surface. SS substrate used was mil finished. Acid treatment makes the surface rougher. SEM analysis was done on treated and untreated stainless steel surfaces. Figure 4-3 shows a SEM image of mil finished SS surface and of acid treated SS surface.
Figure 4.2: Porous geometry in mesh like CNT structures. The above cartoon shows porous geometry in mesh like CNT structures. The structure is modeled using sheets with staggered holes in them. These sheets are then layered on top of each other.

CNT forms mesh like structure on SS due to high roughness on the surface of SS. It was observed that CNT grow perpendicular to the surface where catalyst is adsorbed (Appendix A). Acid treated SS has a highly rough surface. This leads to growth of CNT in random fashion. Figure 4.3 shows SEM image of SS surface used for current work. Figure 4.4 shows SEM image of surface after acid treatment.
Figure 4.3: SEM image of mil finished SS.

Figure 4.4: SEM image of acid treated SS substrate. The surface gets roughened after acid treatment.
The floating catalyst method for growth of CNT is highly versatile and allows us to coat CNT on objects with different shape and size. This is very important for coating SS surfaces to be used in different applications. This method could also be used for coating inner surfaces of pipes. The following optical image shows a 50cm long steel pipe coated with carbon nanotube mesh structure on inside and outside surface using this method [140].

Figure 4.5: Various steel substrates coated with CNT. The above optical image shows objects of various shapes and sizes coated with CNT. (A) Shows an optical image of 50 cm long SS tube coated uniformly with CNT. The tube can be coated on both outer and inner surface. (B) Shows an optical image of CNT coated on different shape of SS substrate.
TEM analysis of CNT grown on SS substrates was done. It was seen that the structure is made of CNT with diameters ranging from 8nm to 20nm. The following Figure shows a TEM image of CNT grown on SS substrate:

![TEM image of CNT grown on SS](image)

Figure 4.6: TEM image of CNT grown on SS.

4.3 Carbon-Nanotube polymer composite structure

Mesh-like CNT structures on SS are made of layered structure, as shown in Figure 4.2. Due to such structure, the individual layers can get peeled off on coming in contact with other surfaces. For use of these structures as coatings, it is essential that they have high mechanical stability. This could be done by binding the layers of CNT together. Polymers were used for binding the layers. It was seen that when a polymer was used to bind these
coatings, polymer would enter in porous structure and would form a thin layer on top of CNT structure. Such behavior lead to loss in superhydrophobic properties and conductivity. It was desired to develop a process such that polymer chains would not fill in the porous structure but would be able to hold different CNT layers together. This could be schematically depicted by Figure 4-7. For this purpose, vinyl terminated poly(dimethylsiloxane) (PDMS) was chosen. PDMS wets CNT [131]. A dilute solution of commercially available PDMS (Sylgard 184) in xylene (1 gm Sylgard in 10 ml xylene) was spincoated on CNT mesh at 2000 rpm for 60 seconds. Spin coating a dilute solution on CNT mesh, dispersed PDMS chains in the matrix. Being very dilute the coating did not form a film on top of CNT. The polymer chains intertwined themselves in CNT network and on the surface of SS. Excess polymer and solvent gets removed due to centrifugal force. PDMS chains were then cross-linked by heating at 70°C for 4 hours. On cross-linking these chains act as a bound to hold the different layers of CNT in place. By using the suitable viscosity of polymer, adhesion of coatings to the steel substrate was increased manifolds without loosing the conductivity of coatings or their superhydrophobicity. SEM images show that the pdms has bound CNT layers.
Figure 4.7: CNT structures held in place by polymer chains The above sketch shows CNT structures held in place by cross-linked polymer chains.
Figure 4.8: SEM image of PDMS impregnated CNT structure.
Figure 4.9: PDMS reinforced CNT structure. The above high resolution SEM image shows PDMS reinforced CNT structure. It can be seen from the image that PDMS hold carbon nanotube layers in place without forming a layer on top of CNT.

To test the fastness of these coatings to the substrate scotch tape test based on ASTM D3359-02 to test adhesion of coating films on metallic substrate was done. In this test pressure sensitive tape is pressed against the coating and peeled off. The amount of coating residue on tape is indicative of how resistant this coating would be to scratching and abrading. Figure 3B shows scotch tape test done on pristine CNT modified steel substrate. It can be seen that a layer of CNT sticks to the adhesive tape and comes out.
Peel Strength: The adhesion of these coatings with the substrate was also tested using a Scotch tape test based on ASTM standard (D3359-02). In this test, the pressure sensitive tape (PSA) is pressed against the coating and peeled off. The amount of coating transferred to the PSA tape after peeling is indicative of the adhesion between the coating and the substrate.

![A](image1.png) ![B](image2.png)

Figure 4.10: Peel test of CNT coatings. (A), (B) Optical images of the pressure sensitive tapes after the adhesion test (based on ASTM D3359-02) done on a pristine CNT-coated steel plate and a CNT-coated SS sample reinforced with PDMS, respectively.

To test scratch resistance of these coatings ASTM D3363-00, Standard test method for film hardness by pencil test was used. In this test graphite pencils of different hardness scale are used to test the scratch resistance of coatings. DERWENT graphic pencils of following specifications were used for the test:

(Softest) 9B-8B-7B-6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H-7H-8H-9H (Hardest)

The 9B was the softest pencil and the 9H was the hardest pencil we have used for these measurements. Pencils were held at 45° angle with respect to the surface normal. The sample was mounted on a sample holder which could move laterally on a rail. Following sketch shows the geometry used for testing scratch resistance.
Figure 4.11: Instrument for scratch test (ASTM D-3363-00). The above sketch shows the geometry used for scratch test measurements based on ASTM standard D-3363-00. The sample to be tested was placed on the sample holder. This sample holder could move on a rail. Different graphitic pencils were loaded on the holder such that the tip of pencil touches the sample surface. This was then followed by moving the sample away from the surface.

The samples were observed using an optical microscope. The pencil which was softer than the coating would leave a graphitic mark on the surface. The pencil which was harder would cut through the coating. This is shown in Figure 4.12.
Figure 4.12: Scratch test of CNT coatings. The above optical image shows CNT coated SS sample tested for scratch resistance. The hardness of pencils increases from left to right. From the image it can be seen that softer pencils left a mark on the sample, whereas harder pencils cut through the coating.

Another important parameter to be measured was electrical resistance of these coatings after reinforcing with polymer. The test method developed was such that it should not pierce through the coating. Figure 4-13 shows the test apparatus used for measuring resistance of coatings.
It was observed that pristine CNT coatings on SS had electrical resistance of order of $10^1$ ohms for a distance of 1 cm between copper plates. If 0.5 gm/ml solution of Sylgard 184 in PDMS was coated on CNT, electrical resistance went up to $10^2$. By increasing the concentration of Sylgard to 1gm/ml electrical resistance of order $10^3$ ohms were observed. From the above we can conclude that there is a tradeoff between electrical conductivity and scratch resistance of coatings. Pristine CNT coatings have high conductivity but low scratch resistance. Coating these structures with variable concentration of PDMS would yield coatings with higher stability but lower electrical conductivity.
Table 4.1: Pristine CNT coatings vs. reinforced coatings.

<table>
<thead>
<tr>
<th></th>
<th>Pristine CNT</th>
<th>Reinforced CNT</th>
<th>PDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Angle</td>
<td>&gt; 160°</td>
<td>150°</td>
<td>≈ 110°</td>
</tr>
<tr>
<td>Resistance</td>
<td>~ 1Ω</td>
<td>~ 100Ω</td>
<td>Resistive</td>
</tr>
<tr>
<td>Scratch Resistance</td>
<td>B-HB (Low)</td>
<td>4H-6H (High)</td>
<td>9H</td>
</tr>
<tr>
<td>Peel Resistance</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

4.4 Wetting

Water contact angle measurements were done on mesh like CNT structures. Deionized water was used for measurement. A 10 μl droplet was placed on the coatings using a micro-liter syringe. Optical image of the droplet was taken using a microscope and contact angle measured. Water formed contact angles of ~170° on CNT coated SS. Water droplet had a very small sliding angle and would roll-off easily at small tilt angles, leaving the surfaces dry.
Figure 4.14: Water contact angle on mesh like CNT coatings. Water contact angle of 167±3 was observed. Water had a very small sliding angle and would roll off at minimal angle. The syringe needle was used to hold the water droplet in place.

The robustness of these coatings under extreme environmental conditions was tested. Four tests were chosen to study the stability of these coatings; exposures to extremely low and high temperatures, boiling water test, and water quench test. The first test involves dipping the CNT coated SS plates in liquid N\textsubscript{2}, until the temperature of plates equilibrated with the temperature of liquid nitrogen. The second test involved heating the plates in air at 300°C for 2 hours. The plates were immersed in boiling water as a third test (for 1 hr). Finally, the plates were immersed in boiling water and then immediately transferred to an ice water bath at 0°C. SEM micrographs were taken after each test to study changes in the structure of the CNT after these harsh treatments. Water contact angles were measured after each test. Figure 4.15 shows one representative SEM micrograph taken after quench test to illustrate that the structure of the carbon nanotube is
intact after the environmental tests. The inset shows water droplet on the steel surface (155-170°), indicating that the surface maintains the hydrophobicity after these tests.

Figure 4.15: Water contact angle on CNT coatings after quenching. Superhydrophobic behavior was observed even after quenching.

It was seen that the structure maintained its superhydrophobic behavior after boiling in water for upto 3 hours. After 3 hours the CNT structure became superhydrophillic. SEM images showed that CNT got clumped after prolonged exposure to boiling water. Figure 4.16 shows the morphology of damaged carbon nanotube structure.
Figure 4.16: CNT structure destroyed by boiling water. It could be seen that nanotubes have peeled off the SS substrate and formed clumps. Such structure would get wet. CNT is slightly hydrophillic, therefore on entering the Wenzel regime, the surface became superhydrophillic. This behavior is irreversible. The stability of these structures could be increased by forming a composite structure using method described in the previous section. Renforced carbon nanotube coatings can sustain boiling water for much longer duration.

When these plates were cooled down to below 0°C, the formation of the ice droplets is much less on the surfaces covered with CNT in comparison to the hydrophilic glass plate. When water was sprayed on the steel surfaces that were kept below 0°C, the droplets freeze with contact angles that are larger than 170°. On heating back the steel plates to room temperatures, the ice droplets melt and the resulting puddle of water rolls-
off the surfaces coated with the CNT. It has been reported in literature that ice repellency of a material increases with higher contact angle. The shear stress value of ice depends on the contact angle hysteresis of water on the material [141,142]. Formation of frost crystals is also lower on superhydrophobic surfaces as compared to hydrophilic surfaces.

![Image of ice droplet on CNT coating](image)

Figure 4.17: Optical image of ice droplet on CNT coating. Water forms spherical droplet on coming in contact with coated ss plated kept at sub-zero temperature. In case of hydrophilic surfaces, water would form a film on the surface before solidification. Such property allows easy removal of ice from superhydrophobic steel surface.

It was also observed that CNT coated SS surfaces retard formation of ice on their surface. To test this property a pristine steel plate and carbon nanotube coated were cooled to sub-zero temperatures in ambient conditions. It was seen that water vapor present in air would condense at much higher rate on non-coated steel plates than on coated steel plates. This is demonstrated in Figure 4-18.
Figure 4.18: Ice-retardation on superhydrophobic SS plate. The above optical image shows ice-retardation of superhydrophobic steel plates. The above Figure shows CNT coated SS plate (A) and a uncoated SS plate (B) kept on a surface cooled using liquid nitrogen. It was seen that ice would start nucleating at higher rates on un-coated steel plates.

4.5 Floatation

Many natural organisms like water strider and water spiders utilize surface tension forces to walk on the surface of water. Water striders have long thin legs which show water contact angle of around 167° and can stand on the surface of water [143]. Inspired from such natural systems floatation behavior of CNT coated SS plate was tested. Such systems could be used for formation of miniature floatation devices.

Conventional floatation devices, utilizing buoyant force require displacement of water mass equivalent to the mass of the floating object. Such systems fail if the density
of the object is greater than that of water. Therefore miniature floatation devises is not feasible using the above principal. Surface tension forces may be utilized in such cases. These surface tension forces depend on hydrophobicity of material. The amount of resistance offered to penetration depends on hydrophobicity of the material. In the case of small superhydrophobic surfaces, the amount of water displaced is much greater than just the volume of object. Thus even a material with density higher than that of water can float on the surface of water. The net upward force acting on the material is a function of the amount of water displaced by the body and the meniscus, plus the net vertical component of surface tension [144].

![Diagram](image)

**Figure: 4.19: Upward force acting on a sphere on water surface. The above sketch shows net upward force acting on a superhydrophobic sphere on water surface. The net upward force is sum of new buoyant force ($F_b$) due to meniscus on water surface and surface tension forces ($F_t$).**

In the past a few attempts have been carried out to mimic the behavior of water striders by making objects fitted with long thin wires coated with hydrophobic material like fluorine compounds. Even though using such materials enabled the synthesis of systems which could stay statically on surface of water, the method lacked miniaturization due to the use of long wires to increase the perimeter [143,145]. Steel
wires used for these experiments had high water contact angle hysteresis. Therefore another shortcoming faced by these systems was that they offered high resistance for pulling out of the surface of water. For an effective floatation device it is desired that maximum payload can be carried in a small volume and the material can be pulled out of water with least possible resistance.

Figure 4.20: Robotic water strider. The above image shows a robotic strider built at Carnegie Melon University, in Metin Sitti’s lab. The strider was formed using 6 stainless steel wires, 14 cm long. The robot can carry approximately 4 gm of payload before sinking in water [145].

The above challenges can be answered by making 2D structures. Maximum payload capabilities of 2D SS structures were measured. Making the substrate thinner reduces the weight of the substrate itself thus allowing higher payload carrying capacity. Stainless steel is the most suitable choice for such application. Steel has a very high modulus, thus steel plates can be made thinner than corresponding plastic materials without compromising on strength. Floatation behavior of carbon nanotube coated SS plates, 0.5 mm thick were tested. The plates of various dimensions were pressed onto the surface of water and maximum force these plates can take before sinking in water was measured. A load cell was used to measure the upward force acting on these plates due to
pressing on water. The load cell has a Wheatstone bridge which is connected to a Keithley sourcemeter.

Samples to be measured were attached to load cell and lowered onto the water surface using a New Focus Pico-meter motor. The motor moved at constant velocity. The force exerted was measured using Keithley 2400 sourcemeter connected to a pc using Rs-232 port and processes using a lab view program. The following diagram shows the setup used to measure force exerted on the plates:

![Setup to measure maximum load before sinking](image)

Figure 4.21: Setup to measure maximum load before sinking. The above sketch shows the setup used for measuring payload capacity of SS plates.
The maximum depth to which carbon nanotube coated stainless steel plates could press on water to create a dimple were measured using optical images. It was seen that plates could press to a depth of 4-5 mm before sinking in water. For a plate of thickness 0.5 mm, it means that it can support 8-10 times its weight before sinking in water surface. This observation concurred with the data of force exerted on plates before they sink in water surface. The following optical images show top and side views of plates pressing on water surface:

Figure 4.22: Superhydrophobic plate pressing onto water surface. Above optical image shows the top view of SS plate pressing onto water surface.
Figure 4.23: Side view of SS plate pressing on water surface.
Figure 4.24: Buoyant force acting on SS plate. The above graph shows the force (mN) acting on the plate as it is being pushed into the water. The bottom red line corresponds to the density of water multiplied by the volume of the plate (buoyancy force). The top red line shows the maximum force supported by plate before sinking. It was seen that superhydrophobic steel plate can sustain ten times higher load than what buoyancy alone would have supported.

Due to high water contact angle carbon nanotube coated steel plated displaced more water than other hydrophobic coatings. The maximum force sustained before sinking was compared for cnt coated steel plate and PDMS coated steel plate. PDMS has a water contact angle of 110°.
Figure 4.25: Buoyant force on PDMS coated vs. CNT coated SS plates. The above graph shows maximum force sustained by PDMS coated SS plate and CNT coated SS plate.

The other advantage of CNT coated system is that it shows less pull down force as compared to other hydrophobic systems when removed from water surface. Lower pull down force is because CNT coated steel lies in Cassie-regime. This behavior could be observed using optical microscope. Figure 4.25 shows an optical image of bottom surface of SS plate being pushed in water surface. It was observed that the bottom part of CNT coated SS plate appeared silvery. This is due to air trapped between carbon nanotube plate and water surface.
Figure 4.26: Air trapped on superhydrophobic surface under water. The optical image showing air trapped on SS surface.

Figure 4.27: SS plate floating on water surface. The above optical image shows a ss plate, 1.3 g heavy floating on the water surface. The hole was drilled in the center of plate to reduce the weight of plate and enhance its payload capacity. Such design could be used for designing water walking robots and miniature floating devices.
Different holes sizes were punched in the stainless steel surface to test the floatation behavior. Figure 4.28 shows four such stainless steel plates tested for floatation.

![Figure 4.28: CNT coated ss plates with different number of holes punched. Total weight sustained before sinking for ss plates with different holes punched.](image)

It was observed that the total force sustained before sinking was same for different SS plates. However by punching greater number of holes in the system the payload carrying capacity could be increased.
The above data shows that the total weight sustained before sinking could be increased by increasing the projected area of the steel plates. The payload carrying capacity can be increased by forming thin perforated systems. Based on this hypothesis a miniature floatation device was formed using helical ss structure. It was observed that optimized geometry of such structure can carry large payload on a small area.

Figure 4.29: Force sustained by plates versus projected area of the plate.
Figure 4.30: Helical SS structure with payload. The above optical image shows a helical SS structure coated with CNT with payload on the surface.

4.6 Heat transfer

Saturated steam is used in many industrial processes to heat fluid running through metal pipes. Metal pipes, when used in heat exchanger applications, may get coated with a layer of water which would then acts as an insulating layer thus reducing heat transfer efficiency. It has been shown that heat transfer efficiency of a material can increase by making its surfaces superhydrophobic [146]. However the coatings used were self assembled layers of organic molecules on Si wafer. These organic coatings have disadvantage of being thermal insulator and being thermally unstable. These coatings can be applied only to high energy surfaces like Si. An effective superhydrophobic coating for heat transfer would include a thermally conductive coating on metal surface.
Mesh like carbon nanotube coatings on steel is one such system. It was shown by Berber et. al, that CNT has unusually high thermal conductivity, [146]. A home built miniature heat transfer furnace was used to compare the heat transfer efficiency of CNT coated SS pipes and uncoated SS pipes (Figure 4-31).

![Diagram of heat transfer furnace](image)

Figure 4.31: Heat transfer furnace. The above sketch shows an assembly to measure heat transfer ability of SS pipes. The system included a glass chamber with sealed ends. The ends could hold SS pipe 1/4” in diameter. The chamber had an inlet for steam and outlets to allow excess steam and condensed water escape the system. Water was flowed through the steel pipe and temperature of water entering and exiting the glass chamber was monitored.

The system was used to study heat transfer rate of CNT coated and uncoated SS pipes. Water at different flow rates was passed through the pipe and let the whole system was allowed to equilibrate for an hour. Table 4-2 shows data for heat transfer of coated and uncoated SS pipes.
Table 4.2: Heat transfer data for CNT coated and uncoated steel pipes.

<table>
<thead>
<tr>
<th>Flow (ml/min)</th>
<th>CNT coated steel pipe</th>
<th>Uncoated steel pipe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$ (°C)</td>
<td>$T_f$ (°C)</td>
</tr>
<tr>
<td>240</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>198</td>
<td>16</td>
<td>37</td>
</tr>
<tr>
<td>155</td>
<td>16</td>
<td>42</td>
</tr>
<tr>
<td>115</td>
<td>16</td>
<td>55</td>
</tr>
<tr>
<td>72</td>
<td>17</td>
<td>77</td>
</tr>
</tbody>
</table>

From the above table it can be observed that heat transfer efficiency of CNT coated pipes is higher than un-coated steel pipes at higher flow rates and is similar to uncoated steel pipe at lower flow rates. The reason behind such behavior can be explained based on residence time of water in steam environment. At higher flow rate residence time of water is very small. In that case difference in heat transfer efficiencies became important. At low flow rates, residence time of water is higher. There is sufficient time for heat to transfer from exterior to interior of pipes. Therefore at low flow rates heat transfer efficiency of both coated and uncoated SS were similar.
Figure: 4.32: Uncoated SS pipe in heat transfer furnace. The above optical image shows an uncoated SS pipe in steam chamber with cold water flowing through. Steam would condense on the SS pipe and form droplets on the surface. These droplets form an insulating layer and reduce heat transfer efficiency of such systems. It was observed that droplets would grow in size and drop under the weight of gravity. Depending on the conditions material thickness of equilibrium water layer formed may be different.
Figure 4.33: CNT coated SS pipe in heat transfer furnace. Optical image of CNT coated SS pipe in steam chamber with cold water flowing through. It was observed that no large water droplets were formed on SS surface.

Conservation of energy is a great need in present times. A few percent increase in efficiency for industrial processes such as heat transfer, can help reduce environmental load tremendously. CNT coated SS plates can provide a solution to this problem. However such systems have a lower stability and the CNT coating gets peeled off by long exposure. The future work would be directed towards stabilizing these coatings.
CHAPTER V
SUMMARY AND CONCLUSIONS

In the current work CNT-polymer composite structures were used to create superhydrophobic materials. The structure of CNT array was optimized to impart functional properties to these superhydrophobic coatings. By combining mechanical properties of micro-patterned aligned CNT array with superhydrophobicity, self-cleaning adhesives were generated (gecko-tape). The structure of these adhesives was inspired from structure found on gecko foot. These adhesive systems combined two contradictory properties, adhesion and self-cleaning, in one system. They not only showed higher adhesive shear strength than natural gecko feet, but also mimicked the remarkable self-cleaning abilities of the gecko and the lotus leaf. These properties could be further enhanced by studying and optimizing the diameter of CNTs, pattern size and spacing between nanotube bundles. The backing material and binding glue may also play an important role in the overall performance.

We showed that gecko tape geometry could be used for creating flexible electron emission devices. The geometry included CNT array partially trapped in a polymer matrix. Embedding carbon nanotubes in polymer matrix helped in counteracting the surface roughness and prevented pullout of carbon nanotubes from the base. The whole geometry could be made flexible or rigid depending on desired application. The main challenge in making the whole system flexible is maintaining distance between the
electrodes. Flexible matrices could buckle from unsupported regions causing short-circuiting.

Mesh-like carbon nanotube structures were used to impart superhydrophobicity to steel surface. These structures had high hydrostatic stability and maintained their superhydrophobicity even after extreme thermal stresses. A process was developed to further reinforce these coatings using polymers, without significantly losing the conductivity and superhydrophobicity. We showed that miniature floatation devices inspired from water strider could be built using such systems. Such principle can help in designing aquatic devices. Being composed of carbon nanotubes these coatings have high thermal and electrical conductivity. Combination of high conductivity and superhydrophobicity made these coatings suitable for heat transfer applications. We showed that mesh like carbon nanotubes coatings on steel pipe could help in enhancing thermal transfer efficiency.

To conclude, superhydrophobic materials with unique functional properties were developed. Synthesis of these materials would help in better understanding of problems like fibrillar adhesion, electron emission and wetting. The future work would include study of wetting behavior of CNT arrays with respect to CNT diameter and modification of these coatings using plasma polymerization technique.
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APPENDICES
APPENDIX A

MULTI-EDGED STRUCTURES

The current section describes aligned carbon nanotube geometries formed by choosing the right substrate geometry. Vertically aligned CNT grow perpendicular to the substrate. In case where multiple surfaces are present CNT would grow perpendicular to all the surfaces. Such structures are very important for applications like fillers. CNT were grown on SiO$_2$ substrates with multiple edges. It was seen that there is explosive growth on the edges. Figures A.1 and A.2 show SEM images of aligned CNT grown on multi edged silicon wafers.
Figure A.1: Shows SEM image of carbon aligned nanotubes grown on silicon wafer with multiple edges. It can be seen from the image that aligned CNT were grown.
Figure A.2: High resolution SEM image of carbon aligned nanotubes grown on silicon wafer with multiple edges.
APPENDIX B

CARBON NANOTUBE FLOWERS

The current section describes flower like geometry of CNT formed by using right combination of carbon source. This geometry was formed by combination of aligned CNT and carbon mat. This carbon mat linked all the nanotubes together and can find applications in composites and for electronics. The mat of carbon was formed by catalytically cracking acetone in the CVD furnace. Acetone forms a thin porous sheet of carbon on silicon wafer. This was then followed by injecting carbon source and metallocene catalyst in the furnace. Vertically aligned CNT grew under the carbon mat. Following Figure shows optical image of this structure:
Figure B.1: Optical image of aligned nanotube-carbon film composite structure. Due to a carbon film on top of nanotube structure, the whole system had high reflectance.

When looked under electron microscope, it was seen that the shiny mat was a thin layer of carbon. The exact structure of this layer could not be determined. Under this structure were vertically aligned CNT. The following SEM images show these structures in detail.
Figure B.2: SEM image of composite carbon structures. In this area it can be seen that the aligned nanotubes punctured through the carbon layer on top. It can be seen that a thin mat like structure if formed on top of aligned carbon nanotube geometry.
Figure B.3: SEM image showing aligned nanotubes with a carbon mat on one end. It formed umbrella like structure.
Figure B.4: SEM image showing that the aligned nanotubes punctured through the mat and emerged out to form flower like structure. The carbon mat peeled off forming petal like structures. The whole geometry looks like flowers of CNT.
Vertically aligned nanotubes were also grown on aluminum substrate. Growing CNT on aluminum will allow direct incorporation of nanotube structures in electronic devices. The growth temperature for growth on aluminum was 640°C, since aluminum melts at 660°C. When xylene was used as carbon source, it was observed that a lot of amorphous carbon would form on the surface due to low growth temperatures. To reduce the formation of amorphous carbon ethyl alcohol was used as the carbon source. Aluminum foils can be very thin and flexible. Therefore growth on aluminum gives us an opportunity to grow nanotubes directly on flexible substrate. Such property is very important for use of as-grown carbon nanotube arrays in flexible microelectronics. Figure 3-19 shows SEM image of carbon nanotube arrays grown on flexible aluminum substrate. Figure 3-20 shows higher resolution SEM image, it can be seen that the nanotube array has grown perpendicular to the substrate.
Figure C.1: SEM image of aligned carbon nanotube structure grown on a flexible aluminum substrate.
Figure C.2: High resolution SEM image of aligned CNT grown on aluminum. The above is higher resolution image of CNT shown in Figure 3-19. It can be seen that aligned nanotube structures are formed. The length of nanotube array is 10 microns.