

## **Supporting Information**

---

### **Tuning the Wetting Properties of Multiwalled Carbon nanotubes by Surface Functionalization**

**Bhalchandra A. Kakade and Vijayamohanan K. Pillai\***

*Physical and Materials Chemistry Division, National Chemical Laboratory,*

*Dr. Homi Bhabha Road, Pune-411 008, Fax: +91 20 25902636, India*

---

---

Author to whom correspondence should be addressed:

[vk.pillai@ncl.res.in](mailto:vk.pillai@ncl.res.in), Fax: +91-20-25882636

\*Corresponding author: Dr. K. Vijayamohanan (Email: [vk.pillai@ncl.res.in](mailto:vk.pillai@ncl.res.in))  
Fax: +91(20) 2590 2636.

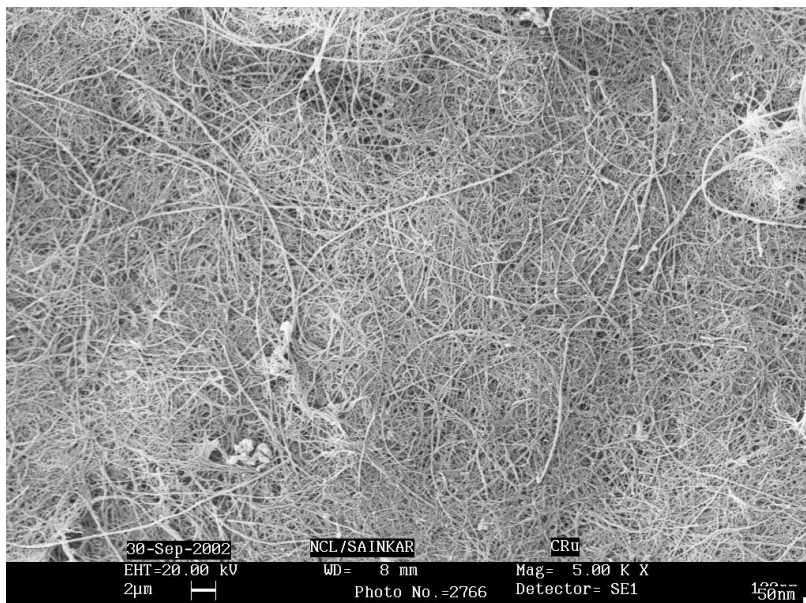
## S1. Experimental:

All MWNT bucky papers have been prepared after appropriate acid treatment mentioned in the following text. All contact angle measurements have been performed on a GBX model (DIGIDROP contact angle instrument) using Windrop software. The contact angle measurements have been performed after fixing the bucky paper (thickness; 0.5 mm) on a glass slide with double side stick-tape with no effect due to the tape. Extreme care has been taken in carrying out these measurements to monitor CA values (standard deviation of  $\pm 2^\circ$ ) at room temperature (27 °C) and constant humidity.

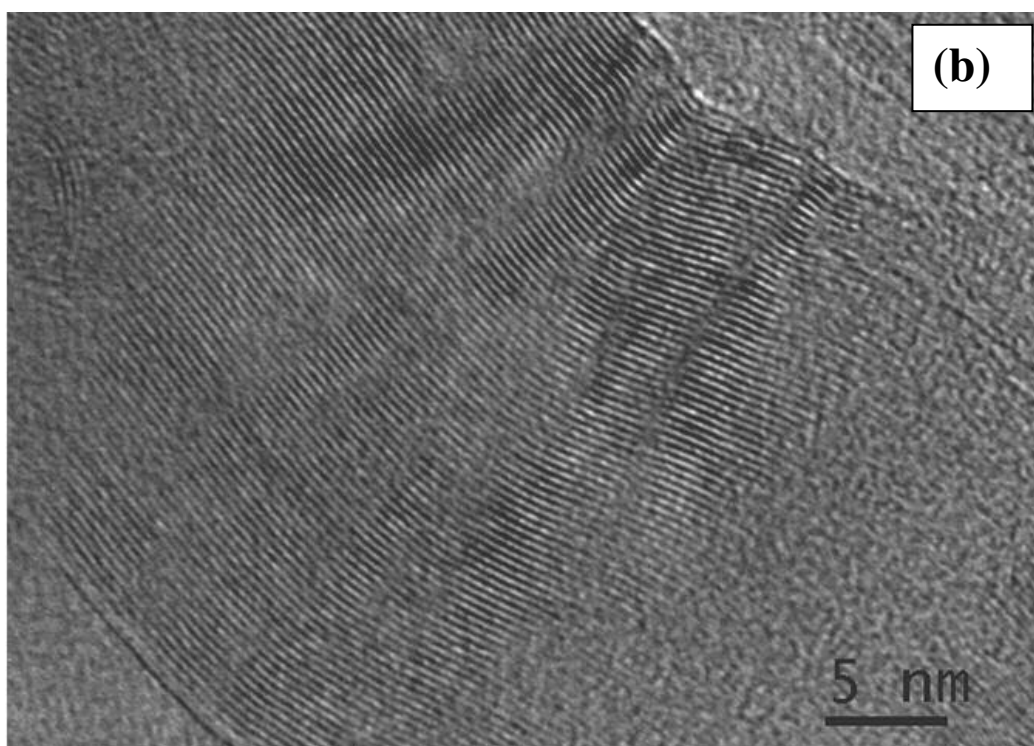
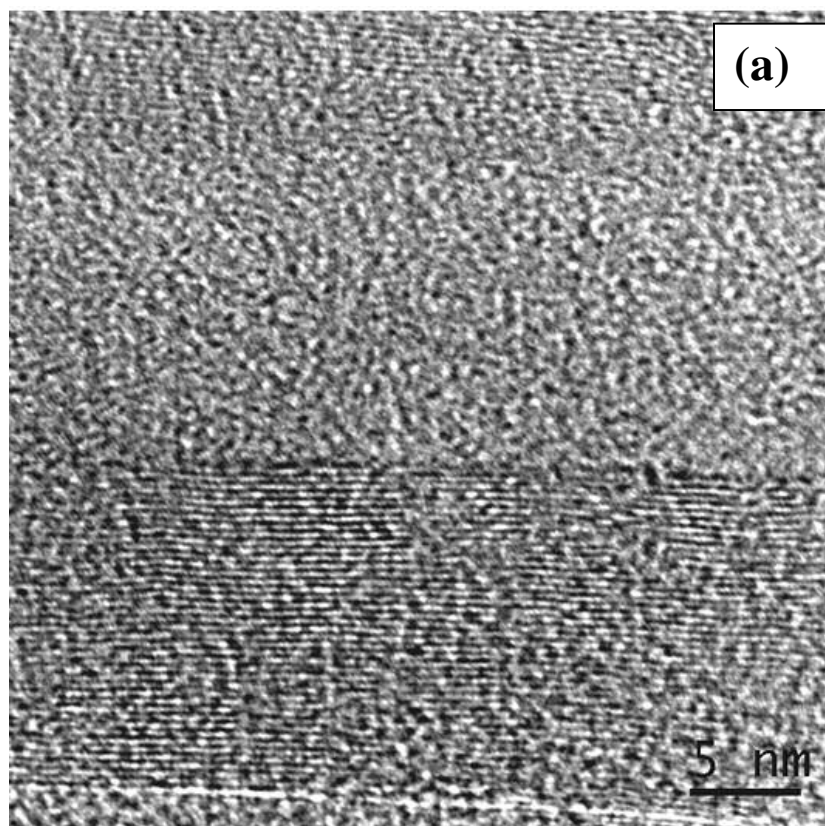
### Experimental procedure for Tuning the Wettability of MWNTs

#### [A] Pristine MWNTs:

MWNTs used here were received from RPI, Troy, New York (synthesized by CVD process; purity >90%) with diameter of 20- 30 nm. It also contains 1% of bigger MWNTs (100-150 nm, determined from TEM analysis)



**Figure S1a.** SEM image of pristine MWNTs



**Figure S1b.** HRTEM images of pristine MWNTs, showing comparatively less uniformity in the lattice fringes and hence the crystallinity

**[B] Ozonolysis:**

About 62 mg of pristine MWNTs soot (above mentioned) were weighed and dispersed in a solution of dichloromethyl (DCM). The solution was sonicated for about half an hour to get a homogeneous dispersion. The dispersion was then put for the ozonolysis reaction in the ozonolysis reactor for about an hour. The reaction was quenched using approximately 2 ml of dimethyl sulphide (DMS). The excess DMS was removed by several washings by DCM and then filtered by the usual procedure. Finally the filtered sample was dried under the IR lamp for twenty minutes.

**[C] Nitric acid treatment:**

20 mg of as received sample of MWNTs was mixed with 40 mL of 3:1 HNO<sub>3</sub> solution. The mixture then was refluxed for 20 hrs at 60°C in an oil bath in order to oxidize the graphitic sp<sup>2</sup> carbon to convert into –COOH, -OH groups on the side walls of nanotubes. The acidified nanotubes were filtered through polytetrafluoroethylene (PTFE) membrane with pore size of 0.2 µm and washed thoroughly using Deionized water. Finally, the carbon film (bucky paper) formed on the membrane was washed with acetone followed by drying at 100 °C in an oven to remove the moisture and used as it is for further experiment.

**[D] High Acid treatment:**

20 mg of as received sample of MWNTs was mixed with 40 mL of 3:1 HNO<sub>3</sub> solution. The mixture then was refluxed for 20 hrs at 60°C in an oil bath in order to oxidize the graphitic sp<sup>2</sup> carbon to convert into –COOH, -OH groups on the side walls of nanotubes. The acidified solution of nanotubes was then kept for 1 month at room temperature. Acidified nanotubes were then filtered through polytetrafluoroethylene (PTFE) membrane with pore size of 0.2 µm under vacuum and washed thoroughly using Deionized water. Finally, the carbon film (bucky paper) formed on the membrane was washed with acetone followed by drying at 100 °C in an oven to remove the moisture and used as it is for further experiment.

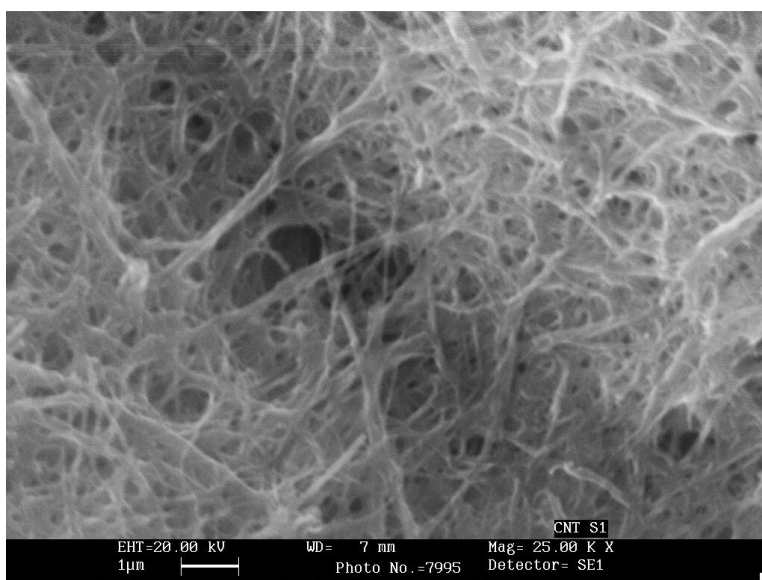
**[E] Acid Mixture:**



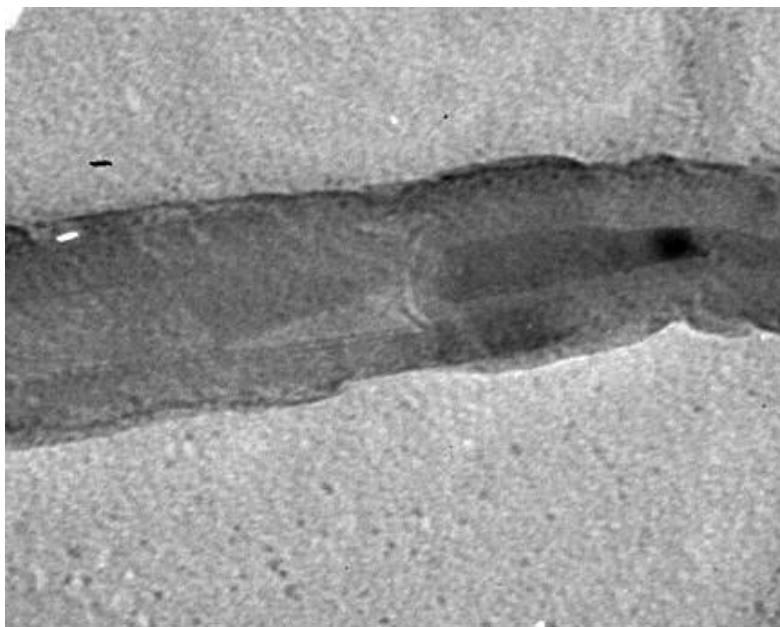
20 mg of as received sample of MWNTs was mixed with 25 mL of 1:1 mixture of 98%  $\text{H}_2\text{SO}_4$  and 78%  $\text{HNO}_3$ . The mixture then was refluxed for 24 hrs at 60°C in an oil bath in order to oxidize the graphitic  $\text{sp}^2$  carbon to convert into  $-\text{COOH}$ ,  $-\text{OH}$  groups on the side walls of nanotubes. The acidified nanotubes were filtered through polytetrafluoroethylene (PTFE) membrane with pore size of 0.2  $\mu\text{m}$  and washed thoroughly using deionized water. Finally, the carbon film (bucky paper) formed on the membrane was washed with acetone followed by drying at 100 °C in an oven to remove the moisture and used as it is for further experiment.

#### [F] TDA-MWNTs:

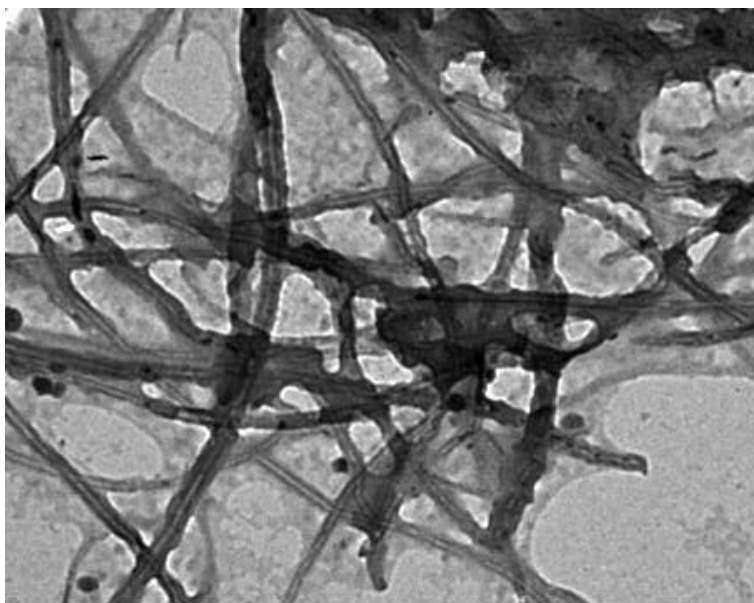
About 40 mg of nitric acid treated MWNTs were mixed with 10 mL of oxalyl chloride and ultrasonicated for 10 mins (taking extreme care during handling of oxalyl chloride) and the reaction was carried out in an argon atmosphere. The mixture was then refluxed for 24 hrs at 60°C to obtain a higher degree of acylchloride functionalization (MWNTs- $\text{COCl}$ ); excess of oxalyl chloride was removed under vacuum using rota-evaporation. MWNTs- $\text{COCl}$  was then mixed with 1 g solid tridecylamine (TDA;  $\text{CH}_3(\text{CH}_2)_{12}\text{NH}_2$ ) and refluxed at 40°C (m. p. of TDA:  $\sim 30^\circ\text{C}$ ) for 40 hrs. The reaction mixture was then cooled and washed with copious amount of tetrahydrofuran (THF) with successive sonication and centrifugation to remove excess of TDA.



**Figure S2a.** SEM images of TDA functionalized MWNTs, revealing a better network of organic TDA wrapped around nanotubes



20 nm



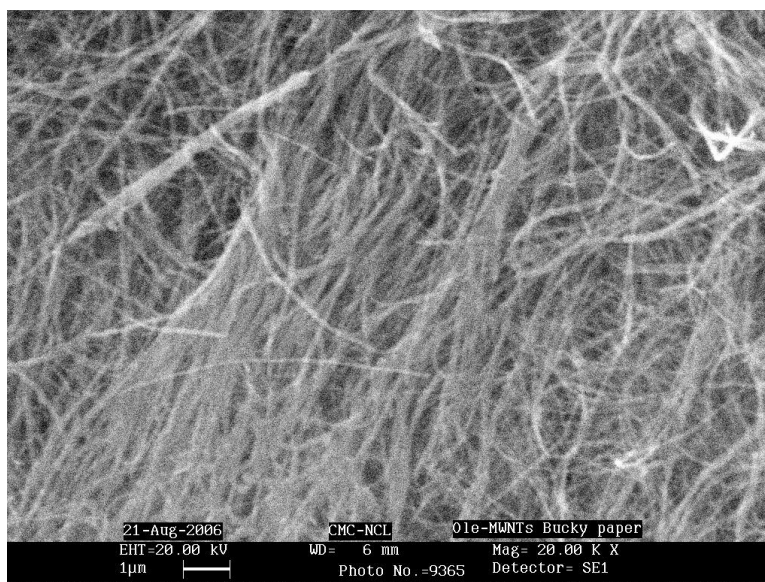
0.5 μm

**Figure S2b.** TEM images of TDA functionalized MWNTs taken at two different resolutions, clearly showing organic wrapping around nanotubes.

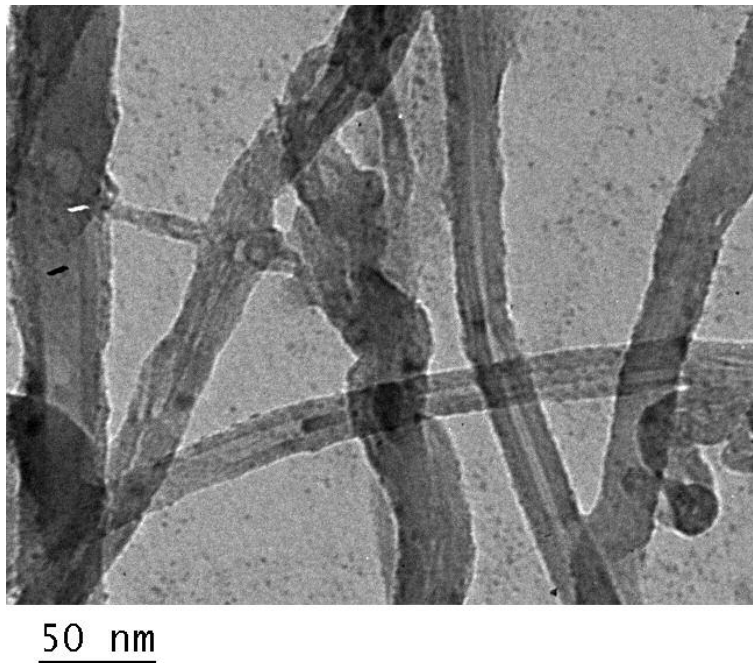
### [G] s-MWNTs

In a typical experiment, 50 mg of MWNT soot was taken in a teflon cylinder with a grooved stopper containing a 1:1 mixture of 98%  $\text{H}_2\text{SO}_4$  and 70%  $\text{HNO}_3$ . This was subjected to microwave (MW) irradiation in a domestic oven for 5 minutes (separated by 60 s off-time interval) using 60% of its total power of 700 W. The rigorous conditions imposed by the MW render rapid breaking of graphitic C=C to develop large amount of –OH, –COO–, –NO<sub>2</sub> and –SO<sub>3</sub>H groups on the sidewalls of the MWNTs. The carbon residue was again dispersed in 3 M HCl and sonicated for 30 minutes to develop –COOH groups rather than –COO–. Acidified nanotubes were subjected to dialysis for 1 day to remove excess of acid content (until the pH of the water becomes neutral). Acidified nanotubes were filtered through PTFE membrane with pore size of 0.2  $\mu\text{m}$  and washed thoroughly using deionized water. Finally, the carbon film (bucky paper) formed on the membrane was washed with acetone followed by drying at 100 °C in an oven to remove the moisture and used as it is for further experiment.

During refluxing with concentrated acids the graphitic surface of the CVD grown MWNTs gets severely damaged (unlike arc-MWNTs), surface gets corrugated, as well surface layers gets fragmented and many cases this causes roughness and mostly  $\text{sp}^3$  disordered type surface is created which is well documented in the literature. This has been confirmed by the HRTEM images as shown in Figure S3c. HRTEM images also clearly suggest severe damage of the side walls which could facilitate the wetting both internally as well as externally. Interestingly, internal wetting would have been observed more effectively, since most of the MWNTs show open ends after microwave treatment.

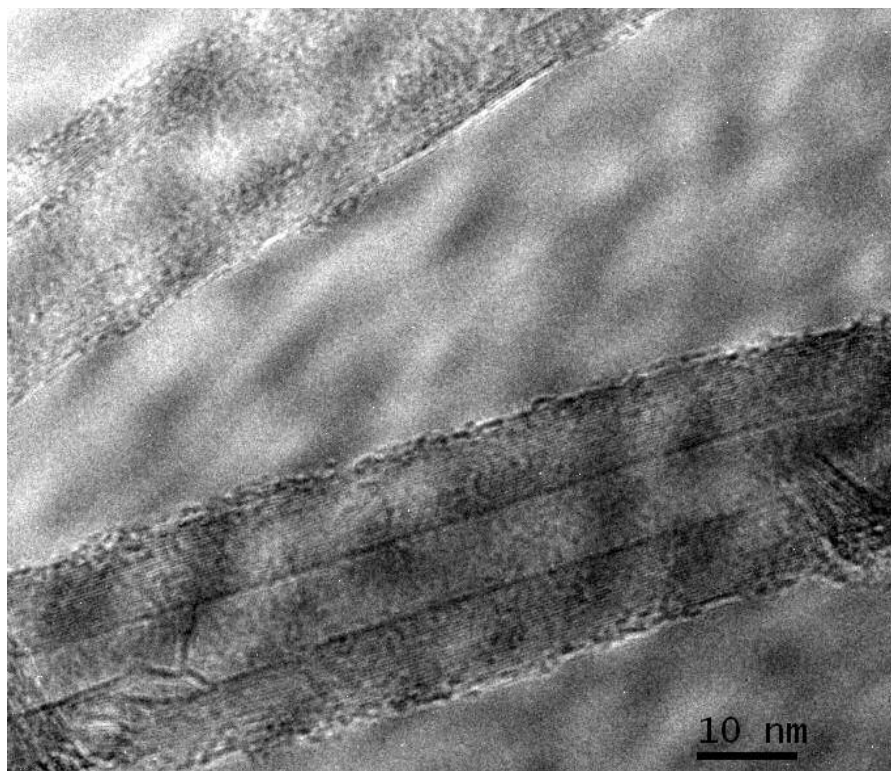


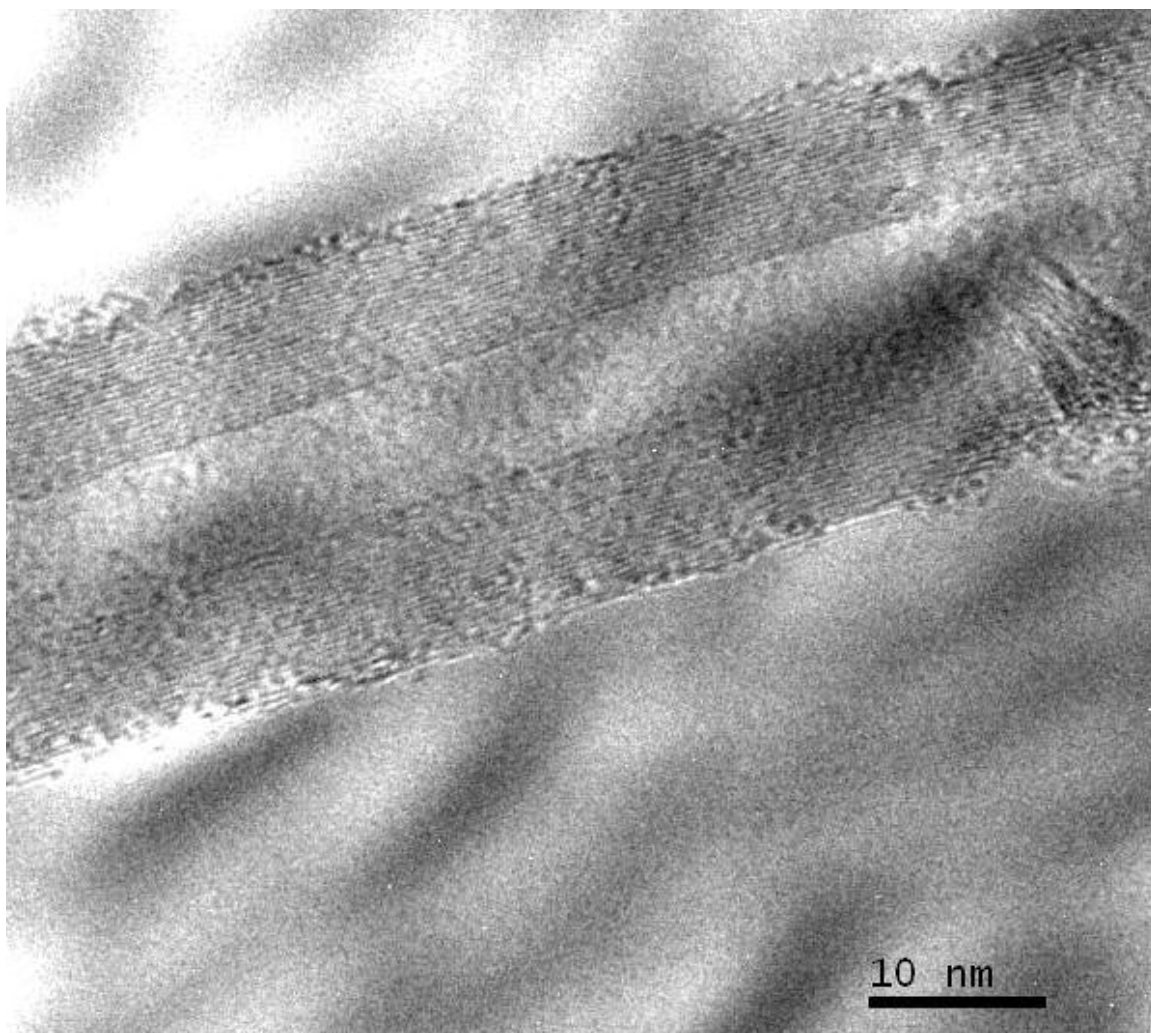
**Figure S3a.** SEM image of microwave (MW) treated (in 1:1 acid mixture) MWNTs, indicating the bundling of nanotubes due to some intertubular electrostatic interaction giving rise to superhydrophilic MWNTs films with CA equals to  $0^\circ$ .

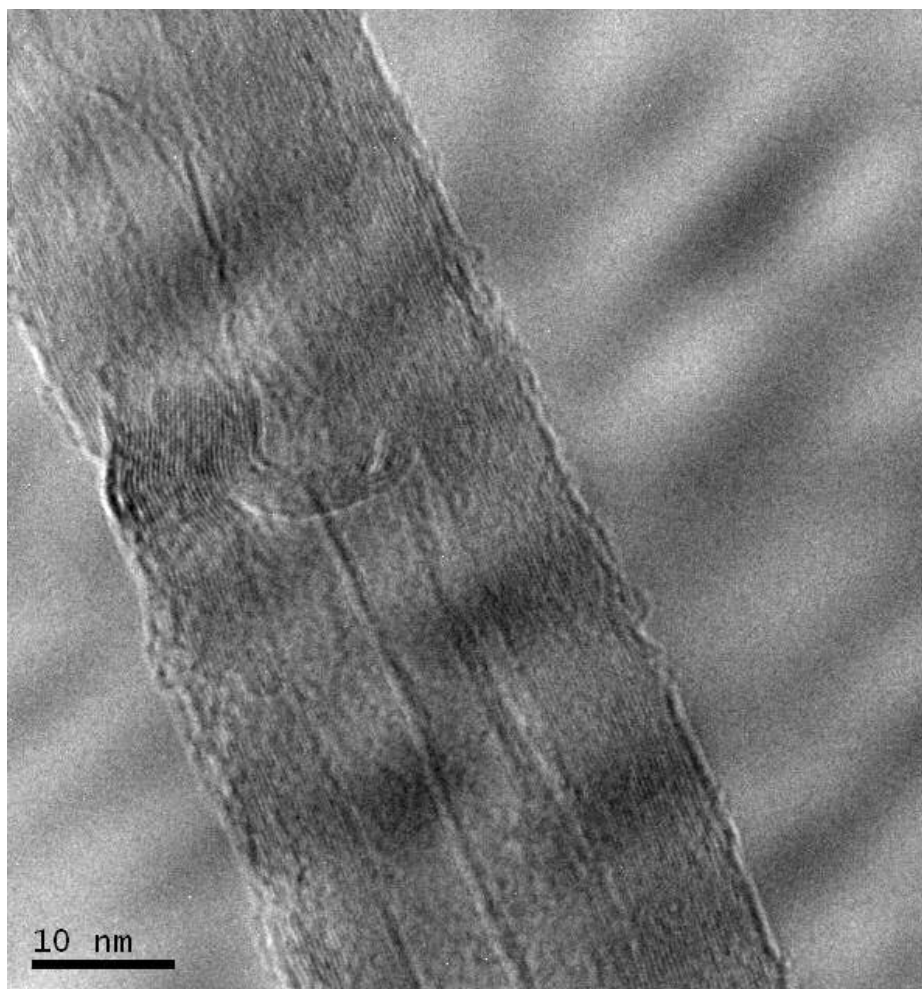




**Figure S3b.** TEM image of microwave treated (in 1:1 acid mixture) MWNTs, showing more side wall defects produced during MW treatment. It also reveals the formation of graphitic nanoparticles (diameter; 4-5 nm).



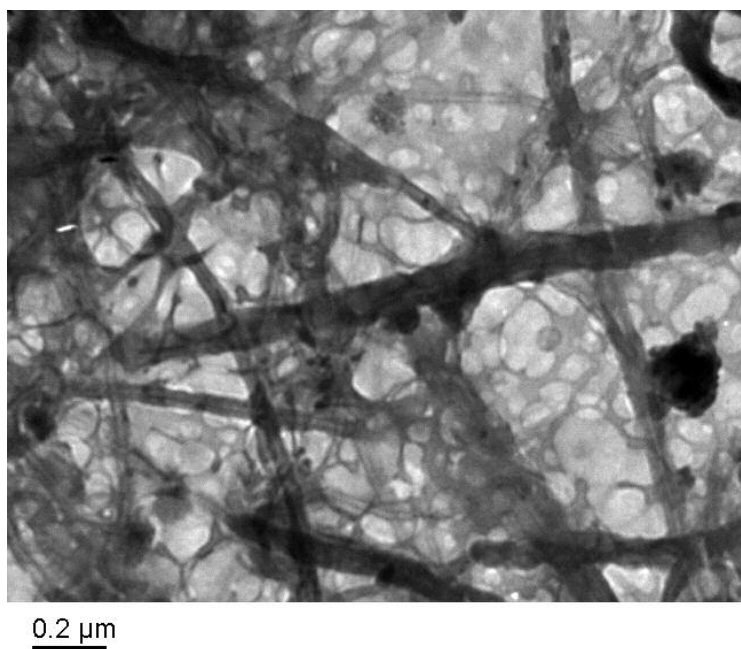




**Figure S3c.** HRTEM images of microwave treated (in 1:1 acid mixture) MWNTs, showing lattice fringes of graphitic nanotubes. It also shows surface corrugation effect, fragmented surface layers causing surface roughness produced during MW treatment.

#### **[H] DAO-MWNTs:**

About 40 mg of nitric acid treated MWNTs were mixed with 10 mL of oxalyl chloride and ultrasonicated for 10 mins in presence of argon atmosphere. The mixture was then refluxed for 24 hrs at 60°C to obtain MWNTs-COCl. MWNTs-COCl was then mixed with 1 g solid 1,2 diaminooctane (DAO;  $\text{H}_2\text{N}(\text{CH}_2)_8\text{NH}_2$ ) and heated at 60°C (m. p. of DAO: ~50-52 °C) for 40 hrs. The reaction mixture was then cooled and washed with copious amount of tetrahydrofuran (THF) with successive sonication and centrifugation to remove excess of DAO.



**Figure S4.** TEM image of DAO functionalized MWNTs, clearly showing organic wrapping around nanotubes.

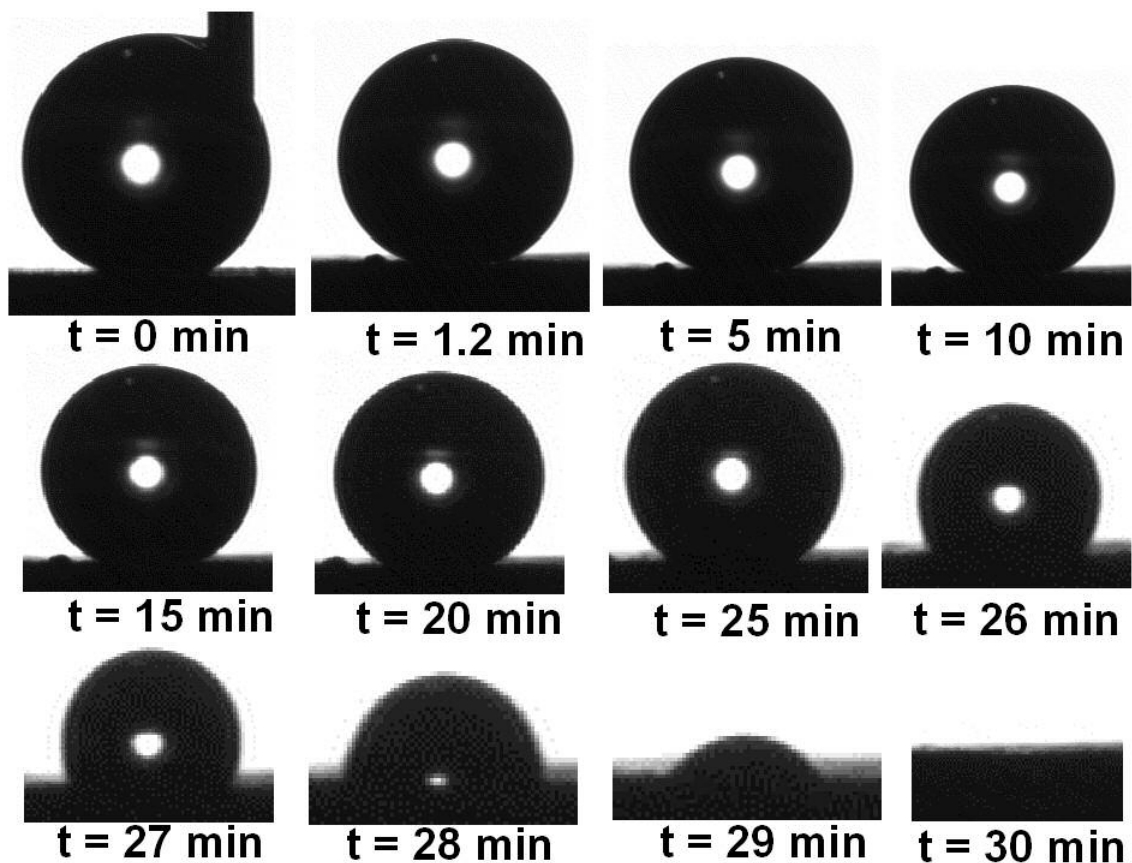
Note:

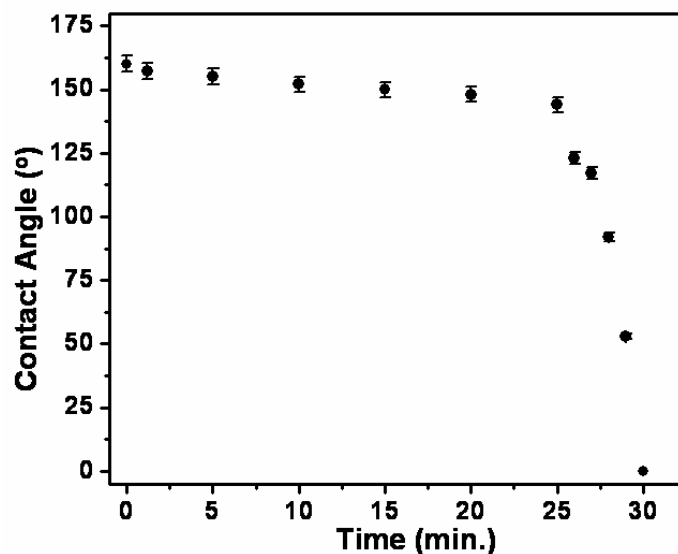
All nanotube samples were dried at 100 °C (in vacuum) in order to avoid the contamination due to moisture (regardless of the removal of some functional groups on condensation) and hence all samples have undergone the same treatment. However, 100° C or more in an oven often removes some of the acidic sites by condensation and hence drying the sample under vacuum at lower temperature may be preferred.



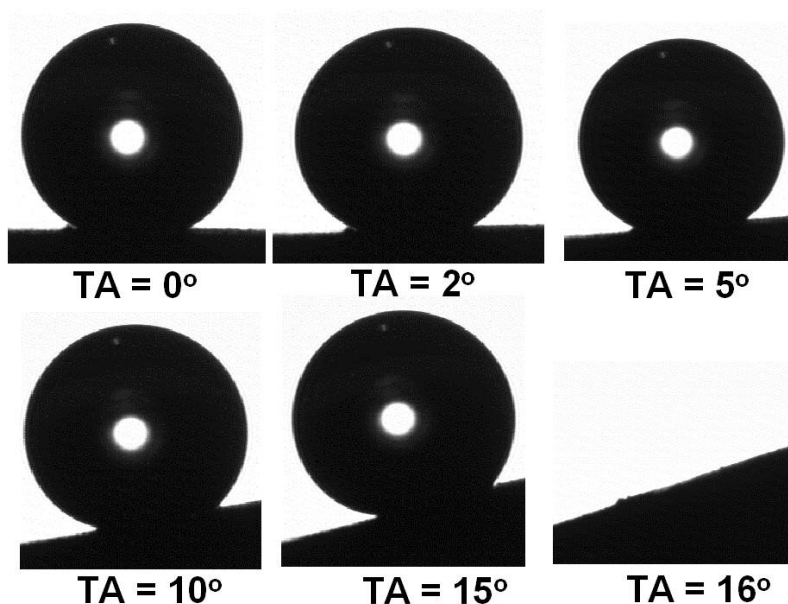
**S2. Water evaporation on pristine MWNTs sample film (water CA profile with time):**

**Figure S5(a)** reveals that, the initial water CA of  $156^\circ$  on pristine sample of (droplet volume;  $4\ \mu\text{L}$ ) evaporates within 30 minutes following constant contact angle (with a very small decrease in CA) until the weight of the drop decreases to an appreciable value and then follows the constant area mode below  $\text{CA} < 90^\circ$ . i. e. initial superhydrophobic surface show a very slight decrease in CA up to 23 - 25 minutes and then suddenly evaporates following constant area mode. These variations in the CA have been recorded at room temperature ( $27^\circ\text{C}$ ) and constant humidity. Interestingly, this super-hydrophobic film (pristine) with an advancing CA for water of about  $156^\circ$  and a roll-off angle for a  $4\ \mu\text{L}$  droplet of about  $16^\circ$  (**Figure S5b**).





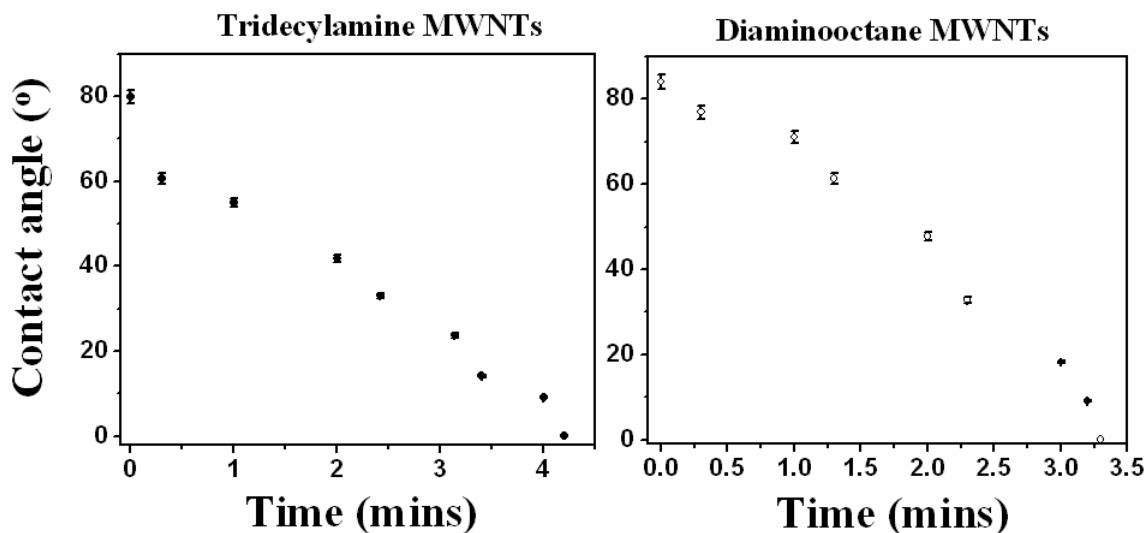
**Figure S 5 (a).** Water drop evaporation profile on pristine MWNTs sample film, recorded at room temperature (27°C) and constant humidity, revealing initial superhydrophobic surface with a very slight decrease in CA (standard deviation  $\pm 2^\circ$ ) up to 23 - 25 minutes and then suddenly evaporates following constant area mode.



**Figure S 5 (b).** Sliding angle measurements shows an initial advancing water CA of about 156° and a roll-off angle for a 4  $\mu$ L droplet of about 16°.

### S3. Contact angle profile on sample F and H:

**Figure S6** indicates the time dependent contact angle ( $\pm 2\%$ ) profile for sample (F) tridecylamine-MWNTs and (H) 1,8-diaminooctane-MWNTs, where the surface of MWNTs is modified by varying the molecular level corrugation associated with different functional groups like  $-\text{CH}_3$  and  $-\text{NH}_2$  created through the amide functionalization.

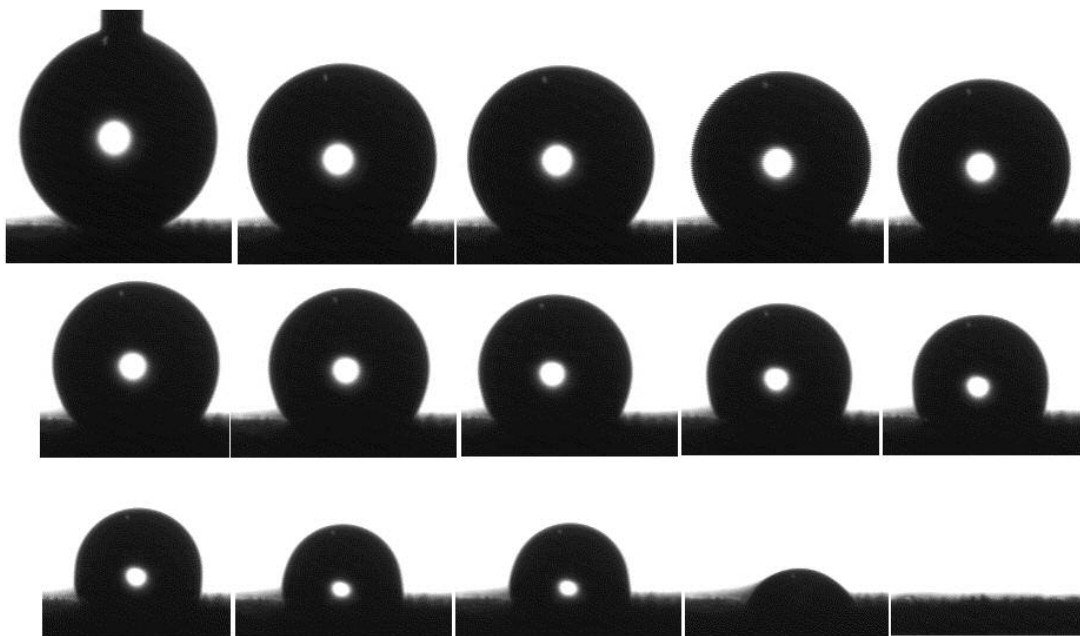


**Figure S6.** Time dependent contact angle profile for sample (F) tridecylamine-MWNTs and (H) 1,8-diaminooctane-MWNTs, showing the drop absorption within 4.2 and 3.3 minutes respectively.

#### **S4. Surface pinning action of MWNTs modified after treatment with 3:1 H<sub>2</sub>SO<sub>4</sub> (I):**

This sample (I; not included in the main manuscript) was prepared by treating MWNTs with 3:1 H<sub>2</sub>SO<sub>4</sub> under microwave irradiation for 4 minutes at a 60% of total power of 700 watts. The initial water CA shows a value of 145° whereas it diminishes to 0° within 6 minutes indicating surface pinning followed by absorption through capillary action (**Figure S7**). In sharp contrast to the pioneering work by Birdi and Vu ([a] K. S. Birdi, D. T. Vu *J. Phys. Chem.* **1989**, 93, 3702-3703 and [b] K. S. Birdi, D. T. Vu *J. Adhesion Sci. Technol.* **1993**, 7, 485-493), it has been found that, the initial water CA of 145° (hydrophobic) diminishes to 0° (hydrophilic) in a linear fashion but follows the constant area mode. These variations could be due to the fundamental drawbacks observed in their studies like, use of different substrates and with varying drop liquids. Hence it could be concluded that, the variation in wetting properties of MWNT bucky paper using such surface designing strategies provides controlled heterogeneity on the surface with no or minimal effect on surface roughness.

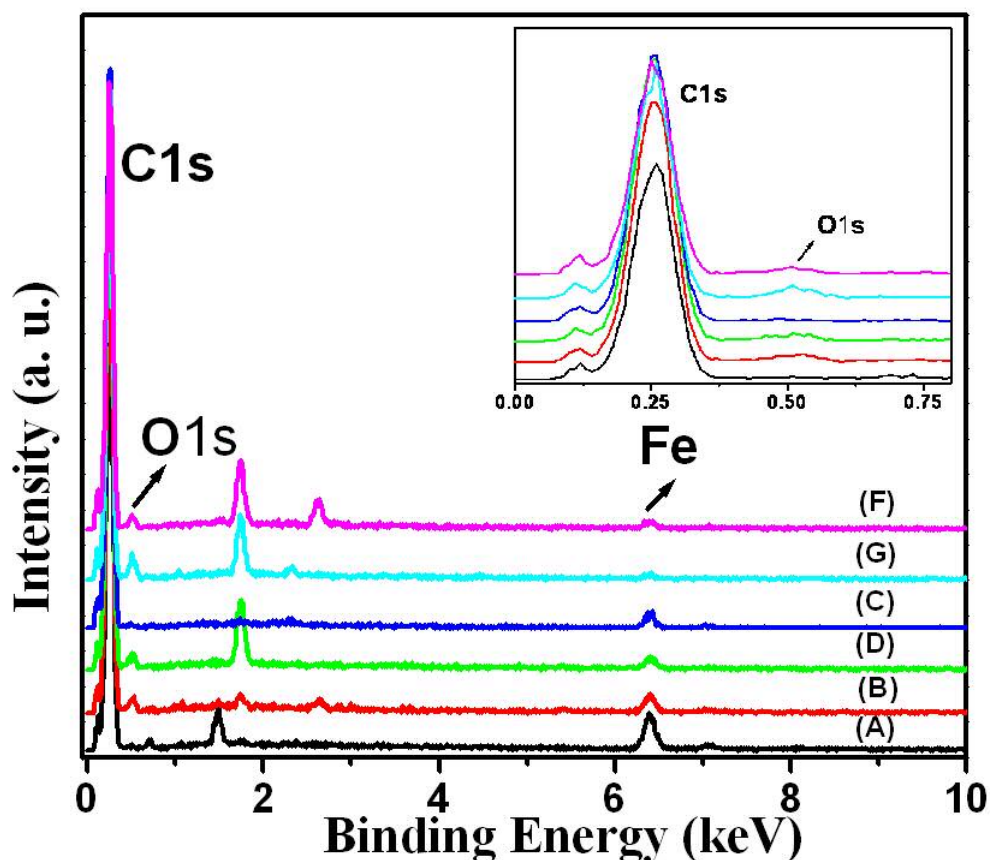




**Figure S7.** Surface pining followed by absorption of water droplet on MWNT bucky paper prepared after modification using treatment with 3:1 H<sub>2</sub>SO<sub>4</sub>. The water droplet absorbs within 6 minutes.

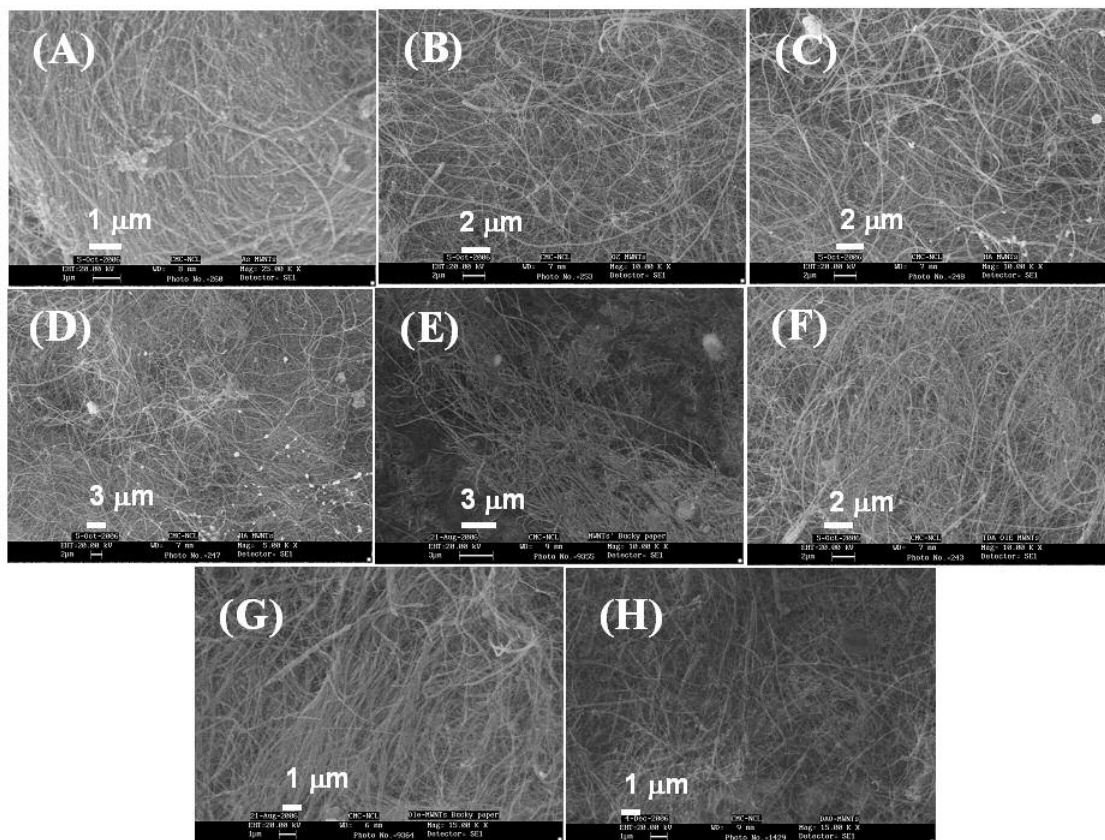
#### S5. Oxygen content on bucky paper sample (using EDX analysis):

**Figure S8** shows the superimposed EDX spectrum of all bucky paper samples, indicating variations in the extent of oxygenated functional groups that determine the surface topography. Among all samples, the sample G shows a maximum amount of oxygen content, which is responsible for its superhydrophilic (contains maximum extent of oxygenated functional groups like  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$  and  $-\text{OH}$ ) nature within 2 seconds.



**Figure S8.** Superimposed EDX spectrum of all bucky paper samples, indicating variations in the extent of oxygenated functional groups that determines the surface topography.

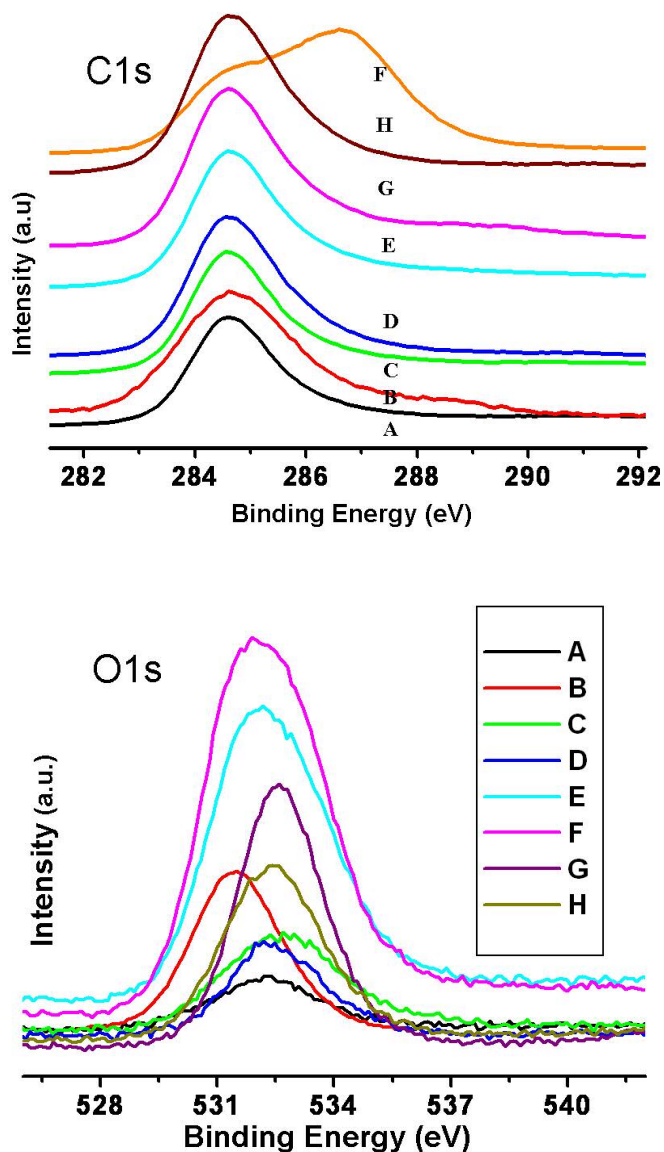
## S6. Surface topography by scanning Electron microscopy:



**Figure S9.** Scanning electron micrographs of pristine MWNTs (A) and modified bucky paper samples (B-H) of MWNTs that shows compact films after modification.

Figure S9 show typical scanning electron microscopic images (A-H) of the surface of samples A to H, which indicate very compact nature of bucky paper (film) clearly showing the difference in the image-contrast due to the variation in conductivities after modification.

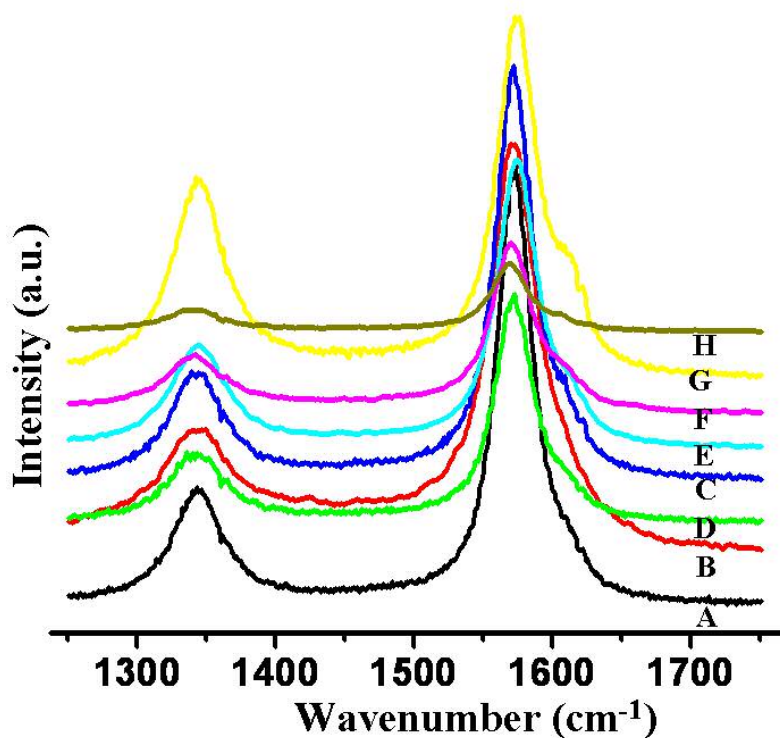
## S7. X-ray photoelectron Spectroscopy



**Figure S10.** Superimposed XP spectra for core level C1s and O1s for all bucky paper samples, revealing a prominent variation in the O1s intensities due to difference in the oxygen content of the surface of nanotubes. C1s peak of sample F is affected seriously due to additional  $sp^3$  carbon chain formed due to the tridecylamine. However, most of the changes have been affected in the O1s peak, where relative variation in the surface oxygenated groups determines the surface property. Therefore, chemical functionalization is the one way to tune the surface wettability of the CNTs.



## S8. Raman Spectroscopy



**Figure S11.** Superimposed Raman spectra for all bucky paper samples, indicating a prominent variation in the G-band (tangential mode) due to difference in surface topography of nanotubes.

The sample G shows an increased ratio of  $I_D/I_G$ , perhaps due to large number of hydrophilic groups like  $-\text{COOH}$ ,  $-\text{OH}$  and  $-\text{SO}_3\text{H}$  produced during pretreatment (microwave in acid mixture for 4 minutes).

### S9. Elemental analysis of all MWCNT samples (C, H, N analysis)

Sample ID	Sample	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
<b>A</b>	Pristine MWCNTs	92.11	0.593	7.297	-	-
<b>B</b>	Oz-MWCNTs	85.42	1.091	13.489	-	-
<b>C</b>	3:1 HNO <sub>3</sub> MWCNTs	84.09	0.900	14.607	0.403	-
<b>D</b>	HA-MWCNTs	83.23	1.000	15.360	0.410	-
<b>E</b>	Acid mix-MWCNTs	80.00	1.800	18.000	-	0.200
<b>F</b>	TDA-MWCNTs	62.27	9.370	16.720	5.510	6.490
<b>G</b>	s- MWCNTs	72.518	1.810	24.460	0.501	0.711
<b>H</b>	ODA-MWCNTs	72.820	3.210	15.500	3.640	4.83
<b>I</b>	3:1 H <sub>2</sub> SO <sub>4</sub> MWCNTs	82.110	-	17.890	-	-

Sample ID	Sample	Treatment	Functional group	Amount of acidic sites (sites/g)
<b>A</b>	Pristine MWCNTs	as synthesized sample	Graphitic C (sp <sup>2</sup> )	-
<b>B</b>	Oz-MWCNTs	ozonolyzed MWCNTs	-COOCH <sub>3</sub>	-
<b>C</b>	3:1 HNO <sub>3</sub> MWCNTs	refluxed in 3:1 nitric acid for 8 hrs	-OH (major), -COOH	<b>5 x 10<sup>20</sup></b>
<b>D</b>	HA-MWCNTs	refluxing and soaking in 3:1 nitric acid	-OH (major), -COOH	-
<b>E</b>	Acid mix-MWCNTs	refluxed in acid mixture (1:1; 78% HNO <sub>3</sub> and 98% H <sub>2</sub> SO <sub>4</sub> )	-OH, -COOH	-
<b>F</b>	TDA-MWCNTs	covalent coupling with tridecylamine (TDA)	-CONH(CH <sub>2</sub> ) <sub>12</sub> -CH <sub>3</sub>	-
<b>G</b>	s- MWCNTs	microwave treatment in above acid mixture for 4 minutes	-OH, -COO- (major), -SO <sub>3</sub> H	<b>20 x 10<sup>20</sup></b>
<b>H</b>	ODA-MWCNTs	covalent coupling with 1,8-diaminooctane (ODA)	-CONH(CH <sub>2</sub> ) <sub>8</sub> -CONH <sub>2</sub>	-

<b>I</b>	3:1 H <sub>2</sub> SO <sub>4</sub> MWCNTs	microwave treatment in 3:1 H <sub>2</sub> SO <sub>4</sub> for 4 minutes	-COOH (major), - OH	
----------	--	---	------------------------	--