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PAPER

Competitive wetting of acetonitrile and dichloromethane in comparison to that of water on functionalized carbon nanotube surfaces

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Differential wetting of pristine and ozonized carbon nanotubes has been studied using solvents like acetonitrile and dichloromethane in comparison to the well-known wetting behavior of water. Based on their unique structural and physical properties, functionalized CNT substrates have been used due to the fact that independent variation in molecular as well as electronic properties could be controlled by understanding the wetting of these liquids on carbon nanotubes (CNTs), both pristine as well as ozone treated. The sensitivity of the wetting behavior with respect to molecular interactions has been investigated using contact angle measurements while Raman and XPS studies unravel the differential wetting behavior. Charge-transfer between adsorbed molecules and CNTs has been identified to play a crucial role in determining the interfacial energies of these two liquids, especially in the case of acetonitrile. Ozone treatment has been observed to affect the surface properties of pristine CNTs along with a concomitant change in the wetting dynamics.

1. Introduction

Carbon nanotubes (CNTs) have interesting mechanical, electrical, thermal and optical properties¹ which make them promising in many applications like medicine, nano-electronics, solar energy storage, ultrahard coatings and so on. But, due to their hydrophobic nature,² limited solubility and poor adhesion on a variety of substrates, it is generally difficult to process them for certain applications. Similarly, processing of CNT-based composite materials involves a homogeneous suspension or an appropriate solution of CNTs and the other phases like a polymer in a common solvent. The problem of limited solubility of CNTs is, therefore, a major concern because of their tendency to exist as bundles as a result of their high surface energy. Although chemical functionalization can alleviate some of these problems to some extent, a proper correlation of the surface modification and solvation behavior is essential. Understanding the interactions of CNTs with various liquids is, therefore, an important topic both from fundamental as well as practical points of view. More importantly, this may be relevant also to analyze fluid flow through microfluidic channels for applications ranging from lab-on-a-chip³ to drug delivery using CNTs.⁴

Consider, for example, the interaction between single-walled carbon nanotubes (SWCNTs) and water, where the extent of the hydrogen-bond in water decreases up to 70% on contact with the CNT surface.⁵ Flow sensors based on the phenomenon of voltage generation upon fluid flow through CNTs have been prepared⁶ and are relevant in applications like MEMS/NEMS and self-cleaning coatings. The carbon nanotube surface is macroscopically rough (although, an ideal, individual graphene surface is not rough) and that leads to its fascinating wetting properties. Chemical functionalization makes its surface more rough and at the same time opens up its tips. Surface modification by chemical reactions, therefore, changes its wetting properties. It has been observed that the surface properties of CNTs with respect to water can be tuned by proper surface functionalization.⁷ Our recent work shows an electric field induced, superhydrophobic to superhydrophilic switching in ozonized MWCNT bucky papers, where a droplet behavior could be reversibly switched from the superhydrophobic Cassie–Baxter to the hydrophilic Wenzel state.⁸ However, water is a unique solvent having high surface tension (72 mN m^{−1}) and dielectric constant ($\epsilon = 80$) facilitating strong hydration interactions. Naturally, there is a quest for understanding the wetting behavior and interaction of liquids having different surface tensions and dielectric constants on CNTs—both on pristine as well as on functionalized. Unfortunately, there are very few reports which can show or predict such wetting behavior or interactions although few theoretical studies show that geometry and properties of acetonitrile molecules trapped inside CNTs differ significantly than those of free molecules and their dielectric constant increases

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significantly as compared to those of free acetonitrile molecules.⁹ This provides a strong motivation to understand the interaction of organic liquids with CNT surfaces so that eventually specific surface functionalization strategies could be tuned for desired applications.

The present work, accordingly, aims to explore the competitive wetting properties of CNTs with two organic liquids, namely acetonitrile and dichloromethane in comparison to our recent studies of wetting with water. Acetonitrile (CH_3CN) and dichloromethane (CH_2Cl_2) have been chosen as model molecules for the study as these two molecules differ in physical (*viz.* dipole moment, surface tension, viscosity *etc.*), molecular and electronic properties. More significantly, these results could be used to compare with the water–CNT interactions. Wetting behavior of the two liquids has been studied by contact angle measurements. FTIR, Raman and XPS have been performed in order to understand the differential wetting of acetonitrile and dichloromethane. Results have been interpreted in terms of molecular interactions between CNTs and the liquids. Both dispersive (non-polar) and non-dispersive (polar) components of the liquids as well as the surface chemistry combinedly have been found to determine such interactions and subsequent wetting behavior. The result of these studies would be useful for a variety of applications including composite materials processing, chemical sensors *etc.*

2. Experimental

2.1 Chemicals

Acetonitrile (CH_3CN , HPLC grade) and dichloromethane (CH_2Cl_2 , AR grade) were purchased from Rankem Co. and purified and dried according to the standard procedures before using for the wetting studies.

2.2 Synthesis and ozonolysis of MWCNTs

Multiwalled carbon nanotubes (MWCNTs) were prepared by a CVD method¹⁰ using a ferrocene and xylene mixture at 700 °C in a tubular furnace in Ar-flow. Ozonolized bucky papers for this study were prepared as described elsewhere.¹¹ In brief, MWCNTs (purity >90%, diameter 20–30 nm and ~1% contains CNTs having diameter 100–150 nm as determined from TEM analysis; not shown), dispersed in dichloromethane (60 mg in 40 mL CH_2Cl_2), were subjected to ozonolysis in a suitable reactor (Fischer Ltd.) for about an hour, quenched with dimethyl sulfide (2 mL), washed with dichloromethane and subsequently filtered and dried at 80 °C under vacuum (this ozonized sample is denoted as oz-MWCNT while the pristine sample is described as p-MWCNT). Finally, the dried material was pressed at 0.2 bar pressure to obtain bucky papers (60–80 μm thick).

2.3 Contact angle measurements

All contact angle measurements were performed on a GBX model (DIGIDROP contact angle instrument) using Windrop software. The sessile contact angle measurements were performed after fixing the bucky paper (thickness; 60 μm) on a clean, dry 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 contact angle values within 1–2 min to avoid the evaporation effects. All contact angle measurements were carried out at room temperature (27 °C) and constant humidity (40–50%) with a standard deviation of $\pm 2^\circ$.

2.4 FTIR analysis

In order to understand the presence of various functional groups on the side walls of nanotubes, before and after functionalization, FTIR studies have been performed using a Perkin Elmer instrument-Spectrum One FTIR spectrometer in the diffused reflectance (DRIFT) mode, after a thorough mixing of a small amount of sample in dry spectroscopic grade KBr followed by drying in a desiccator for 24 h.

2.5 Raman spectroscopy

All Raman spectroscopy measurements were carried out at room temperature on an HR 800 Raman spectrophotometer (Jobin Yvon Horiba, France) using monochromatic radiation emitted by a He–Ne laser (632.8 nm) operating at 20 mW. The experiment was repeated several times to verify the consistency of the spectra. The samples were prepared simply by putting a drop of the desired liquid on p-CNT or an oz-bucky paper.

2.6 X-Ray photoelectron spectroscopy

X-Ray photoelectron spectroscopic (XPS) measurements were carried out on a VG Micro Tech ESCA 3000 instrument at a pressure of $>1 \times 10^{-9}$ Torr (a pass energy of 50 eV with an electron take off angle of 60° and an overall resolution of 1 eV) using Mg K α (source, $h\nu = 1253.6$ eV) radiation. The alignment of binding energy (BE) was carried out using Au 4f binding energy of 84 eV as the reference. The X-ray flux (power 70 W) was kept deliberately low to reduce the beam-induced damage. The spectra were fitted using a combined polynomial and the Shirley type background function.^{12,13} For recording XPS p-MWCNTs were dipped in acetonitrile for 2 days and were taken out before loading into the instrument.

2.7 Scanning electron microscopy

The morphology of the MWCNTs was examined by a LEICA Stereoscan 440 scanning electron microscope (SEM) equipped with Phoenix energy dispersive analysis of X-ray (EDX).

2.8 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out on a TGA Q5000 TA Instruments-Thermal analyzer from 50 °C to 900 °C at a rate of 10 °C min⁻¹ in air as well as in nitrogen. Both p-MWCNTs and oz-MWCNTs were soaked in dichloromethane and acetonitrile for 2 h prior to TGA measurements.

2.9 Conductivity measurement

The electrical conductivities of the p-MWCNT and oz-MWCNT were measured at room temperature using a four-point probe method employing a constant current source (mA) and a microvoltmeter keeping the distance between probes as $0.2 \pm 2\%$ cm. A bucky paper of thickness 0.121 mm for oz-MWCNTs was used for conductivity measurement while p-MWCNTs were dropcasted from an isopropanolic suspension

on a cover slide and dried in the oven. The thickness of the coating was 0.02 mm.

3. Results and discussion

3.1 FTIR analysis

Fig. 1 presents the FTIR spectral changes of the MWCNT sample before and after ozonolysis. The spectral bands originating at frequencies 1736 cm^{-1} , 1262 cm^{-1} , 1110 cm^{-1} are indicative of ester group formation. The band at 1736 cm^{-1} is assigned to the C=O group and those at 1110 and 1262 cm^{-1} are due to the C–O stretching. The peak at 1596 cm^{-1} is the stretching frequency of the C=C group located near the newly formed oxygenated groups. The peak at 3436 cm^{-1} is assigned to adsorbed atmospheric moisture. All peaks are in accordance with the previously reported works.^{14,15}

3.2 SEM analysis

Fig. 2 presents a comparative analysis of the scanning electron micrographs of p-MWCNT and oz-MWCNT. Interesting change in the contrast for the image of oz-MWCNTs indicates

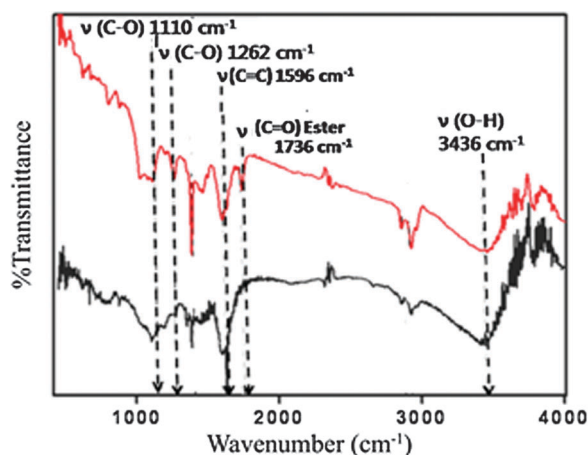


Fig. 1 Infrared modes resulting from the ozonolysis of MWCNT. Ozone exposure causes outerwall functionalization which results in the formation of C–O, C=O groups. Frequencies of the vibrations for these groups are indicative of the formation of ester linkages on the outerwall of CNTs.

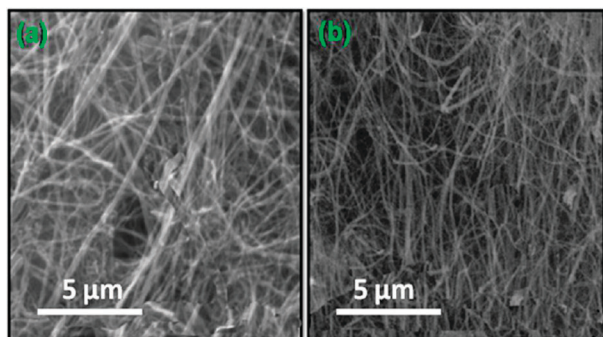


Fig. 2 Scanning electron micrographs of (a) pristine MWCNT and (b) the bucky paper after subjecting the MWCNTs to ozonolysis.

the formation of surface functionality on exposure to ozone. Also the images show more compactness of the bucky paper as compared to that of p-MWCNTs. During ozonolysis the long CNTs break down into smaller fragments, but that is not clear from the SEM images which are limited due to their low resolution.

3.3 Electrical conductivity

Electrical conductivity measurement gives 0.057 S cm^{-1} for p-MWCNT and 1.364 S cm^{-1} for oz-MWCNT paper respectively. This apparently contradicts the general perception that conductivity should decrease upon functionalization (especially ozonolysis) since functionalization introduces some oxygen containing functional groups on the CNT surface consuming carriers. However, this might be true only for individual CNTs but in a macroscopic ensemble, CNTs exist as bundles so that the conductivity is really an average value. CNTs are closely packed with a very little intertubular gap after functionalization. Ozonolysis removes amorphous carbon impurities (which are less conducting and contribute to the overall conductivity of p-MWCNTs) and opens up the upper walls of CNTs giving access for the electrons to pass through the CNTs through the open sites. All these facts render the oz-bucky paper more conducting than that of p-MWCNT. This indirectly gives evidence about the compactness, robustness and mechanical integrity of the bucky paper after ozone treatment.

3.4 Wetting study

Wetting behavior of acetonitrile and dichloromethane on MWCNT surfaces has been depicted in Fig. 3 along with that of water for comparison. Surface roughness is a contributing factor in these experiments. Hence, it has been tried to keep macroscopic surface roughness at its minimum by pressing each sample between two glass-plates, and thus it was almost same for each sample, although it is difficult to control the microscopic roughness all the time. Fig. 3 shows that water does not wet the surface of both pristine as well as ozonized MWCNTs and the contact angle values are invariant with time,

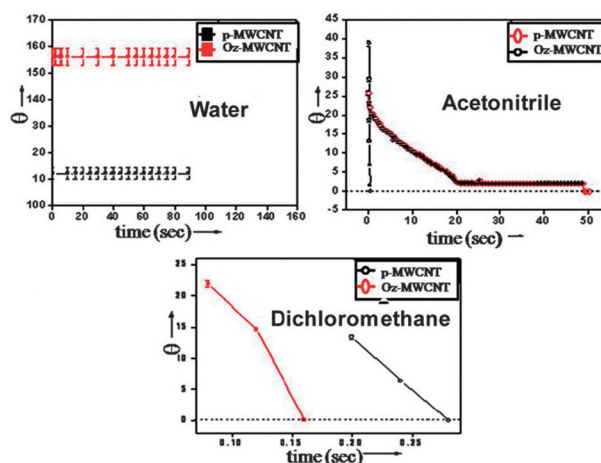


Fig. 3 Wetting behavior of water (H_2O), acetonitrile (CH_3CN) and dichloromethane (CH_2Cl_2) on p-MWCNTs as well as oz-MWCNTs (error bar = $\pm 2^\circ$).

although oz-MWCNT shows superhydrophobicity with contact angles $\sim 158^\circ$ – 160° unlike 112° – 114° for p-MWCNTs. This superhydrophobicity has been attributed in part to the more compact nature of the oz-CNT paper with very small pore sizes and also due to the generation of hydrophobic ester groups which repel the water and cause it to bounce back from the oz-CNT surface.⁸ High surface tension of water (72 mN m^{-1} at 20°C) is another factor for this contact angle variation. Water is a highly polar liquid (6.2 D) and exists as a network of water molecules through H-bonding and not as discrete water molecules. Naturally, it has a very low value of the dispersive component and that is why it cannot penetrate through the intertubular gaps of CNT bundles (both p- and oz-MWCNTs) resulting in a non-wetting situation. The ester group derived from the ozonolysis further restricts the penetration of water molecules and causes superhydrophobicity. Acetonitrile (CH_3CN), on the other hand, completely wets the CNT surfaces. However, the wetting process shows interesting dynamics on p- and oz-MWCNT surfaces. As Fig. 3 suggests, acetonitrile shows time dependent wetting on p-MWCNT. Accordingly, there is a gradual but steady decrease in the contact angle of acetonitrile from an initial value of $ca. 25.8^\circ \pm 2^\circ$ over a period of $\sim 50 \text{ s}$ in the case of pristine-MWCNT (p-CNT) until it reaches 0° (complete wetting). But the contact angle of acetonitrile abruptly decreases from an initial value of $38.9^\circ \pm 2^\circ$ to 0° almost immediately ($< 1 \text{ s}$ from the moment of droplet dispense of the drop) on oz-MWCNT (instantaneous wetting). Parallel but distinctly different behavior is observed also in the case of wetting by dichloromethane (CH_2Cl_2), although the dynamics is pretty fast ($< 400 \text{ ms}$) for both p-CNT and oz-CNT unlike the case for acetonitrile. Instantaneous contact angles in these cases are $13.4^\circ \pm 2^\circ$ and $21.8^\circ \pm 2^\circ$ for p-CNT and oz-CNT respectively. The surface tension of acetonitrile (19.10 mN m^{-1} at 20°C) is less than that of dichloromethane (26.50 mN m^{-1} at 20°C). This means that acetonitrile should spread more rapidly than dichloromethane on the CNT surface, *i.e.*, with lower contact angle than dichloromethane according to Young's equation,

$$\cos \theta_e = \frac{\gamma_{SV} - \gamma_{LS}}{\gamma_{VL}}$$

where γ_{SV} , γ_{LS} and γ_{LV} are the solid–vapor, liquid–solid and liquid–vapor surface tensions, respectively, and θ_e is the apparent contact angle (experimental contact angle). Hence, the different wetting behavior cannot be explained solely by taking into account the surface tension and the capillary effect. In practice, the solid–liquid interfacial energy (γ_{LS}) is governed

by many forces like van der Waals, hydrogen-bonding, dipolar *etc.* and that determines the spreading of a liquid over a surface. Actually, the interactions of the liquids with the CNTs seem to be responsible for those interesting wetting dynamics in the case of dichloromethane and acetonitrile (though it is difficult to draw a molecular level picture by observing macroscopic property like apparent contact angle, a probable interpretation can be obtained by combining with other experimental data like spectroscopic evidence and so on). Dichloromethane is a relatively less-polar liquid with a very low dipole moment of 1.60 D as compared to that of 3.92 D in the case of acetonitrile. Theoretical calculations suggest the dispersive components of 17.0 and 15.3 and a polar component of 7.3 and 18.0 for dichloromethane and acetonitrile respectively. This means dispersive forces are more pronounced in dichloromethane. On the other hand, dipole–dipole interactions prevailing in acetonitrile are revealed from X-ray diffraction and that results in a zigzag chain of acetonitrile molecules by an antiparallel dipole–dipole interaction.¹⁶ This situation is, thus similar, although little different, to the long network of water molecules. Due to this more dispersive nature than acetonitrile, dichloromethane exists as discrete molecules which are much smaller in size than the dimension of the intertubular gaps and, therefore, can penetrate more easily into the intertubular gaps of the CNT papers and thereby results in instantaneous wetting both in the case of p-CNT as well as oz-CNT unlike the situation for acetonitrile. Now, the change of the mode of wetting on two surfaces (p-CNT and oz-CNT) can be rationalized in terms of the opening of the tips of CNTs caused by the oxidation during ozonolysis in the case of oz-CNT. Liquids can easily penetrate into the channels of oz-CNTs through the open tips and that probably is observed as instantaneous wetting. Somewhat higher momentary contact angle in the case of oz-CNTs than p-CNTs can be understood by the momentary hindrance or hydrophobic interaction of the liquids ($-\text{CH}_3$ in the case of CH_3CN and $-\text{CH}_2$ for CH_2Cl_2) with the dangling $-\text{COOCH}_3$ groups which causes superhydrophobicity in the case of water droplets.⁸ The value of the contact angle (instantaneous contact angle) is more for acetonitrile than for dichloromethane because the $-\text{CH}_3$ group is less polarizable and hence more hydrophobic than the $-\text{CH}_2$ group. This may also be due to the more compact interconnected nature of the bucky paper obtained after ozonolysis of MWCNT. The wetting behaviors have been summarized in Table 1, which shows comparative values of contact angles for water, CH_3CN , CH_2Cl_2 (both initial and final) and thus reflects the different types of interactions.

Table 1 Variation in the contact angle of acetonitrile and dichloromethane on pristine and ozonized MWCNTs

Name of the liquid	Surface tension (γ)/ mN m^{-1} at 20°C	Initial value of the contact angle/ $^\circ$	Final value of the contact angle/ $^\circ$	Time of measurement/s	Time for complete spreading/s
<i>(A) Pristine MWCNT:</i>					
Water (H_2O)	72	114	114	90	Does not spread
Acetonitrile (CH_3CN)	19.10	25.8	0	90	50
Dichloromethane (CH_2Cl_2)	26.50	13.4	0	90	0.28
<i>(B) Ozonized MWCNT:</i>					
Water (H_2O)	72	158–160	158–160	90	Does not spread
Acetonitrile (CH_3CN)	19.10	38.9	0	90	Instantaneous
Dichloromethane (CH_2Cl_2)	26.50	21.8	0	90	0.17

3.5 Raman analysis

In order to understand the competitive wetting behavior in terms of specific interactions of acetonitrile and dichloromethane with CNTs, Raman spectroscopic studies have been performed immediately following the wetting of CNTs by the liquids. Accordingly, Fig. 4(A) shows the micro Raman spectra of p-CNT and oz-CNT samples. However, after ozone treatment, G-band intensity drops down significantly ensuring the breaking of the graphitic structure during ozonolysis. As a result, the I_D to I_G ratio increases from 0.61 to 0.76 on ozonolysis indicating more defect formation (more sp^3 than sp^2 carbons as compared to p-MWCNT) on the walls of MWCNTs and thereby causes changes in its electronic structure. In comparison Fig. 4(B) and (C) represents the micro Raman spectra of p-MWCNT and oz-MWCNT after the wetting experiment by acetonitrile and dichloromethane. Raman spectra show a D and a G band shift of $\sim 13\text{ cm}^{-1}$ and 4 cm^{-1} on wetting by acetonitrile and dichloromethane, respectively, in the case of p-CNTs. Interestingly, there is no such shift in the case of oz-CNTs. Moreover, acetonitrile causes an upshift while dichloromethane causes a downshift of the corresponding bands of p-CNTs. Indeed, D (defective) and G (graphitic) are two tangential modes of phonon vibrations in CNTs and these two modes are characteristics of sp^3 and sp^2 type of C–C bonding respectively. A shift in the positions of these bands thus really indicates vibrational energy transfer between CNTs and the liquid molecules.

Many types of experimental evidences suggest a shift in Raman band positions of CNTs on charge transfer to or from the CNTs (as a result of doping).^{17,18} In the case of p-type doping, electrons are taken away from the CNT and thereby

causing an upshift of the band while similar n-type doping pushes charges on CNTs causing a concomitant downshift in both D and G bands. However, CNTs are a huge reservoir of mobile π -electrons and acetonitrile (CH_3CN) having the $-\text{C}\equiv\text{N}$ π -bond can interact with this π -cloud through π - π interaction. The non-bonded electrons on the N-atom can also be donated to the CNT and this causes n-type doping of CNTs and that is manifested in the form of redshift in D and G frequencies from their original position in CNT on wetting by acetonitrile. This is confirmed from the value of the shift ($13\text{ cm}^{-1} = 0.002\text{ eV}$) which is equivalent to the interaction energy for the weakly adsorbing acetonitrile molecules. It has been shown that binding energies for a benzonitrile molecule to SWCNT and a graphene surface vary from 0.01 eV to 0.06 eV depending upon the orientation of the benzonitrile molecule with respect to the SWCNT or the graphene surface (*i.e.*, π - π or π - $\text{C}\equiv\text{N}$ interaction).¹⁸ Acetonitrile (CH_3CN) having no benzene ring for strong π - π interaction like benzonitrile (PhCN) can only interact *via* the $-\text{C}\equiv\text{N}$ π -bond or the nitrogen lone pair and that explains the low binding energy for CH_3CN unlike benzonitrile. It thus appears that acetonitrile molecules form a thin film on CNT after spreading and transferring vibrational energy electronically to the CNTs affecting a change in the vibrational frequency of the CNTs. A dichloromethane (CH_2Cl_2) molecule, however, does not have any charge transfer component to interact like CH_3CN and vibrational bands (Raman bands), therefore, are not affected significantly (Fig. 7). Interestingly, there is no change in the position either of the D or G band on wetting by both of the liquids (Fig. 4(B)). This is somewhat contradictory to a recent report by Nelson *et al.*¹⁹ where molecules inside the CNTs are more efficient in transferring vibrational energy to the CNTs than the molecules around it, because after ozonolysis the shorter and open-ended CNTs can allow the solvent molecules (CH_3CN and CH_2Cl_2) to go in. Moreover, covalent functionalization disrupts the π -clouds and the possibility of π - π interaction reduces and so there is little or almost no change in the D or G band positions in the case of oz-MWCNT even with CH_3CN .

3.6 X-Ray photoelectron spectroscopy

In order to get better insight into the nature of interaction between acetonitrile and CNTs, an XPS study could be very useful. Accordingly, Fig. 5 shows the N1s core level spectrum after acetonitrile adsorption on CNTs. The spectrum suggests that the amount of nitrogen is extremely less. This appears true when we consider weak adsorption of acetonitrile and so, very few molecules present during the experiment (leaving behind non-interacted acetonitrile). Hence, the XPS spectrum of N1s is so noisy. However, deconvolution gives two peaks at 398.1 eV and 400.0 eV. The nitrogen of CH_3CN has a binding energy of 399.4 eV.²¹ The first peak (398.1 eV) may be assigned to the N-atom of some loosely-adsorbed acetonitrile while the second peak at higher binding energy indicates electron donation from the N-atom of the CH_3CN molecule to the CNT whereby the N-atom becomes electron deficient and so there is an upshift of N-binding energy. However, it is difficult to conclude from these experiments whether acetonitrile

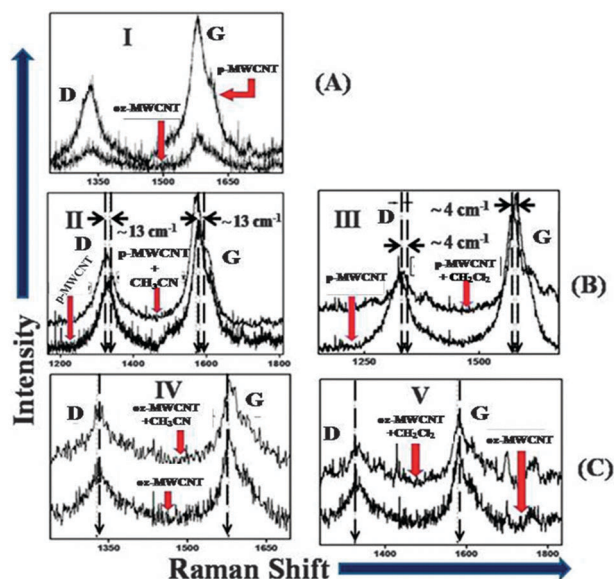


Fig. 4 (A) Superimposed micro Raman spectra of pristine (p-MWCNT) and ozonized (oz-MWCNT) carbon nanotubes showing the rupture of the C=C backbone during ozonolysis to form $-\text{COOCH}_3$ groups. (B) and (C) Micro Raman spectra during the wetting experiments by acetonitrile and dichloromethane respectively. Acetonitrile on (II) p-CNT and (IV) oz-CNT and dichloromethane on (III) p-CNT and (V) oz-CNT measured using a 632.8 nm laser.

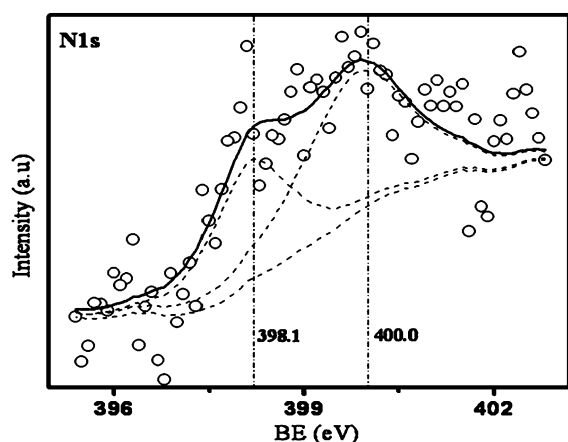


Fig. 5 Core level N1s spectrum showing the interaction of acetonitrile with CNT.

interacts *via* π - π interaction or directly *via* the donation of an unshared electron. This interaction also explains the slow change in the contact angle for p-MWCNT when a drop of acetonitrile is put on its surface. Dichloromethane, on the other hand, cannot interact in such a way because it neither has π -electrons to interact nor unshared electrons to donate and also it is less polar in nature so that it cannot induce charge transfer to or from the CNTs. Thus dichloromethane gets very weakly adsorbed on the CNT surface to cause physical dampening of the phonon modes of CNTs which is supported by the minor upshift (4 cm^{-1}) of D and G band frequencies upon wetting. In sharp contrast, for oz-MWCNT, such type of explanation no longer holds good partly because of the opening of the tips of CNTs after ozonolysis and partly because of the fact that the π -electron cloud on CNT gets reduced on ozonolysis due to formation of more sp^3 carbon atoms on its surface at the cost of sp^2 carbon atoms. The open tips allow easy percolation of the liquids inside the channels and therefore result in observed wetting dynamics.

The surface energy of the p-MWCNTs and oz-MWCNTs have been obtained from experiments and employing Owens-Wendt two component theory.²¹ Accordingly, p-MWCNT has a surface energy of 36.7 mN m^{-1} which could be further decomposed into 9.2 mN m^{-1} polar and 27.5 mN m^{-1} dispersive or non-polar components. The surface energy of MWCNTs decreases to 17.9 mN m^{-1} upon ozonolysis. Polar and non-polar contributions to this surface energy are 4.2 and 13.7 mN m^{-1} respectively. Interestingly, the polar part of the surface energy decreases from $\sim 25\%$ to $\sim 23\%$ and at the same time the non-polar or dispersive component of the surface energy increases from $\sim 75\%$ to $\sim 77\%$ after ozonolysis. This result justifies the fact that there is a less probability of polar interactions between acetonitrile (more polar than dichloromethane) and oz-MWCNT unlike that with p-MWCNT. This might be a probable reason for instantaneous wetting of oz-MWCNT with CH_3CN unlike the case for p-MWCNT. Assuming a uniform inner diameter of MWCNTs and a zero contact angle between inner walls of the capillary and water, we can use the relationship,

$$\gamma = (1/2)\rho g r [h + (r/3)]$$

where, γ = surface tension of acetonitrile and dichloromethane (19.10 and 26.50 mN m^{-1} respectively), ρ = density of the liquid ($\text{CH}_3\text{CN} = 782.2\text{ kg m}^{-3}$, $\text{CH}_2\text{Cl}_2 = 1326\text{ kg m}^{-3}$), $g = 9.81\text{ m s}^{-2}$, r = average inner radius of the CNTs = 3 nm , h = capillary rise. For CH_3CN , $h = 1.65\text{ }\mu\text{m}$ (approx.) and for CH_2Cl_2 , $h = 1.35\text{ }\mu\text{m}$. This capillary rise can be correlated with the opening of the CNT tips and liquid (CH_3CN and CH_2Cl_2) penetration through the CNT channels.

3.7 Thermogravimetric analysis

Thermogravimetric analysis was carried out in order to understand the adsorption-desorption behavior of CH_3CN and CH_2Cl_2 on p-MWCNTs and oz-MWCNTs.

Accordingly, Fig. 6 shows a comparison of thermograms of p-MWCNTs and oz-MWCNTs in a nitrogen atmosphere after soaking in acetonitrile and dichloromethane respectively. Thermal profiles of p-MWCNTs and oz-MWCNTs (in N_2 as well as in air) have also been incorporated for comparison. Interestingly, the %weight of both p- as well as oz-MWCNTs is found to increase after soaking in the respective solvents and the decrease in weight starts at much higher temperature as compared to the reference samples. However, the nature of the plot and the amount of the %weight loss are not the same for

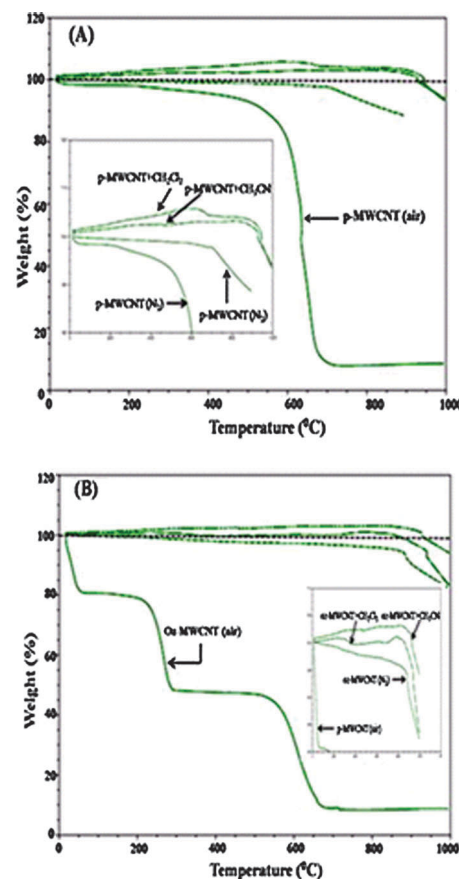


Fig. 6 Thermograms of (A) pristine MWCNTs and (B) ozonized MWCNTs after soaking and heating in dichloromethane and acetonitrile. All measurements were performed in a nitrogen atmosphere. TGA of p-MWCNTs and oz-MWCNTs in air are incorporated in the figure for comparison. Inset shows the enlarged view of the thermograms after soaking in acetonitrile and dichloromethane.

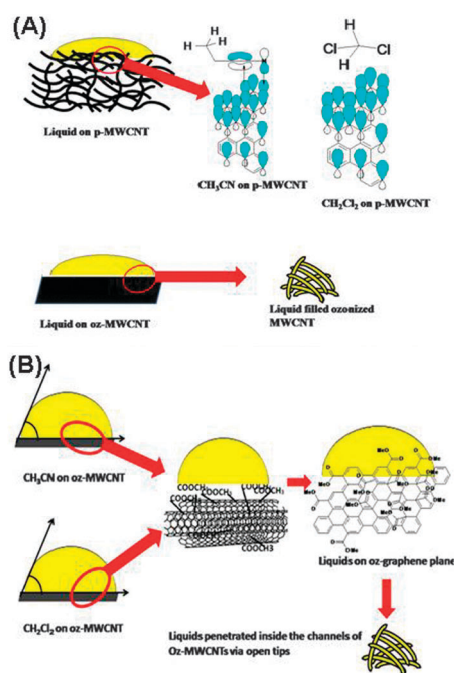


Fig. 7 Interaction of (A) acetonitrile and (B) dichloromethane with CNT.

samples soaked in CH₂Cl₂ and CH₃CN and the difference is more significant for p- and oz-MWCNTs. This clearly indicates the different types of adsorption for the two liquids on CNTs and moreover the nature of adsorption seems to change with the ozone treatment. One probable reason could be the chopping of CNTs upon ozone treatment and thereby facilitating some liquids to get incorporated into the capillary of CNTs and those liquids may get desorbed at higher temperature or react with CNTs resulting in the initial weight increment in TGA (for p-MWCNTs it is mostly the liquids at the interstices of CNT bundles which might react with CNTs).

4. Conclusions

Interaction of acetonitrile and dichloromethane with multi-walled carbon nanotubes has been studied in comparison with the case for well known water–CNT interactions. Although weak interactions of the two molecules with MWCNT surfaces cause variation in their wetting behavior over both pristine as well as oz-MWCNTs, there are critical differences. Experimental evidence predicts electronic interaction in the case of acetonitrile, whereas dichloromethane gets physically adsorbed. Functionalization dramatically changes the wetting behavior of the CNT surface irrespective of the molecular nature of the liquids. Finally, it can be concluded that dipole

moment, surface tension, viscosity *etc.* also play important roles in determining the nature of the wetting dynamics on CNTs. Acetonitrile can interact with CNTs by π – π interaction as well as with the N-lone pair to cause a downshift of the D and the G band of CNTs in the respective Raman spectra (Fig. 7). The results of the studies are believed to be very useful for understanding the interactions between CNTs with liquids relevant for various applications such as supercapacitors, microfluidics, electronics, biosensors and smart composites.

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