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Wettability property of CNT-graphene like film deposited by microwave plasma enhanced vapor deposition technique

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ABSTRACT

Wettability property of carbon nano-tubes (CNT)-graphene like films have been investigated. In this work, we have studied the wettability of CNT-graphene like film deposited on Ni substrate by Microwave Plasma Enhanced vapor deposition Technique (MWPECVD). Compared to the water contact angles of 77.8° for bare Ni substrate, the water contact angle of the CNT-graphene like hybrid films is found to be 128.4°. The nanostructures have been deposited at fixed pressure of 20 Torr with different temperature of 500, 600 and 700 °C. The results indicate that wettability properties of nano-structure can be tailored, significantly. The solid surface energy (SE) of composite films was estimated using contact angle measurements. The wettability of CNT-graphene has been studied first time in film form.

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KEYWORDS
MWCNT; Graphene; Hybrid film; MWPECVD; contact angle; Raman spectroscopy

1. Introduction

The wettability of any thin is very important property, which is governed by its chemical composition and surface microstructures. According to contact angle of a water, a surface may be defined as hydrophilic or hydrophobic surface. If the contact angle is less than 90° it is termed as hydrophilic and if the contact angle is greater than 90° it is called as hydrophobic surface, accordingly. Researcher have great interest to develop hydrophobic surface as it has self-cleaning, waterproof, anti-contaminating nature. Nature have already developed such hydrophobic surface as found in lotus leaves, which is caused by the hierarchical roughness of the leaf surface from micrometer-sized papillae having nanometer-sized branch like protrusions and the intrinsic material hydrophobicity of a surface layer of epicuticular wax.[1] The two-factor affecting the wettability property of any surface are surface area of microstructures and rough-ness.[2]

Carbon-based nano-materials have emerged as extremely promising materials for various types of applications owing to their outstanding electronic optical and mechanical properties. Recently carbon based hydrophobic films have been developed, which in, turn will improve their application in conductive-transparent films, oil-water separation, and electromagnetic-interference-shielding and in other fields.[2–4] Wettability properties of two carbon allotropes CNTs and graphene have been studied individually, yet there are is few literatures available for CNT-graphene hybrid film. The hybrid film as advantage of owing properties of both the allotropes. Carbon nano material have both the required properties to have hydrophobic nature viz. high surface area and roughness Graphene has high surface area; the theoretical specific surface area of graphene is 2630 m^2 g^{-1}.[3] Lee et. al. have deposited CNTs on SS by thermal CVD and found water contact angles of 145–150°.[5] The wettability properties of graphene strongly depend on number of layers and surface microstructures. Graphene as advantage of having high surface area. The as-prepared graphene samples have typical specific surface area ranging from ∼100 to ∼1000 m^2 g^{-1}.[6] The low experimental value of surface area of graphene is due to strongly dependence on layers and structure. Dong et. al.,[4] have measured the contact angle of graphene ∼89.4°, which is not hydrophobic. Shin et al.[7] prepared single, bi and multi-layer graphene by epitaxial method which have water contact angle compared to graphite (∼92°), while Wang et al. reported that the water contact angle of graphene films produced by chemical exfoliation is 127°.[7,8] The contact angle has been improved to 108.5° for 3 D graphene. Shin et. al., have studied wettability properties of epitaxial graphene and found the contact angle 92°, which changes to hydrophilic due to defects as defects increase the surface energy of graphene.[7] The inclusion of CNTs matrix into graphene can improve wettability properties with its roughness due to nano texture.

In the present study, wettability properties of CNT-graphene-like hybrid film with one step deposition by MWPECVD have been investigated. Only a few reports are available for wettability of CNT graphene samples.

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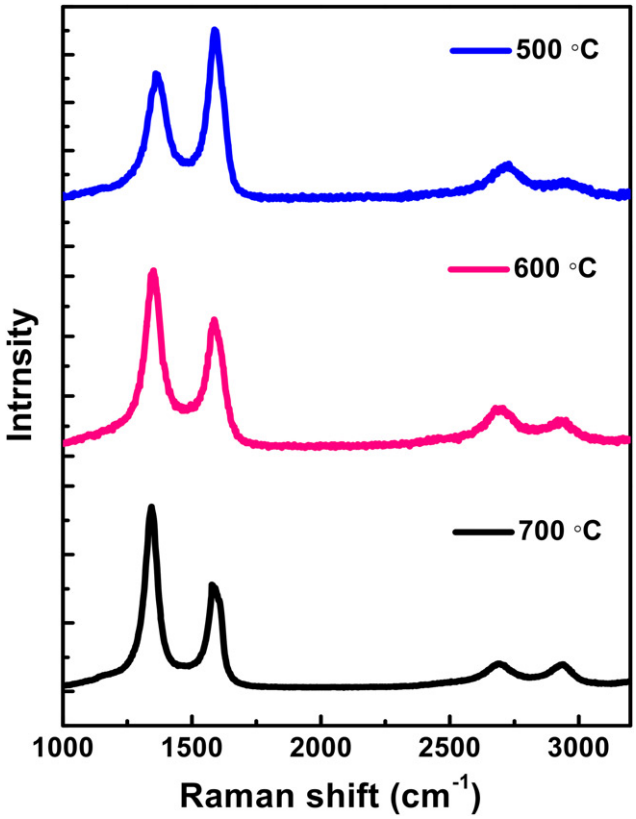

Figure 1. Raman Spectra of CNT-graphene hybrid film deposited at 500, 600 and 700 C.

2. Experimental technique

MWCNT-graphene-like hybrid films were directly deposited on nickel substrates in a custom designed and indigenously developed 2.45 GHz MW PECVD system equipped with substrate heating facility. Nickel substrate (~1 cm^2) were cleaned with help of isopropyl alcohol (IPA), acetone for 5 min and were treated by plasma before deposition. The samples were heated to required temperature, with the heating rate of ~30 °C/min. The pressure was increased up to the desired deposition pressure 20 Torr using H_2 and CH_4 gas mixtures using a throttle valve. After the H_2 plasma pretreatment, the precursor gases, CH_4, H_2 and Ar were allowed into the chamber to attain certain pressure and adjusted the microwave power to sustain the plasma while depositing the thin film for 5 minutes. Static water contact-angle measurements were performed by placing droplets of de-ionized water on the various CNT graphene-like film. Contact angles in the present work were recorded on the Drop Shape Analysis System, model DSA10MK2 from Krüss GmbH, Germany. The image of static contact angle was taken within 4 seconds of liquid deposition by a charge coupled device (CCD) camera.

3. Result and discussion

3.1. Raman spectra

Raman spectroscopy is an important tool to characterized carbon-based nanostructures. Figure 1 shows Raman spectra of the sample deposited at 500, 600 and 700 °C. All samples are showing namely D, G, 2 D and D + G peaks. The position of peaks is shown if Table 1. For single layer graphene 2 D peak appear in range 2650 ~ 2700 cm^{-1}, as no of layers are increased the 2 D band at lower wavenumber depicts the presence of CNTs along graphene-like film.[9,10] Shifting occur in hybrid films due to the p-stacking interaction between the carbon atoms from the graphene sheets and the side-walls of CNTs, due to change in the electronic environments of both graphene and Nanotube.[11] The peak at 1590 cm^{-1} is called Raman-active G band which is, originated from the in-plane vibrational mode. The peak at 1353 cm^{-1} is termed as disorder induced D band, which is originated in the first-order scattering process and usually thought to be due to the presence of in-plane substitutional heteroatoms, vacancies, grain boundaries, or other defects, all of which lower the crystalline symmetry.[12] the D band disappears in the case of highly ordered pyrolytic graphite HOPG, and only the G band exhibits in the fundamental region between 1100 and 1700 cm^{-1}. D peak also represents amount of defects qualitatively. High intensity of D peak is due to presence of CNTs and due to plasma exposure of graphene film. In the region of the higher-order Raman spectrum, three distinct peaks are attributed to combinations of the Raman fundamentals, 2693 (2D), 2937 and D + G, cm^{-1}. These bands have also been appearing in the Raman spectra of HOPG. 2 D band, very sensitive to stacking of graphene sheets, is the overtone of the D band and appears in the second-order Raman spectra of crystalline graphite.[13] Figure 2 depicts the mapping of sample for D and G band. Intensity variation of D and G band confirms the uniformity of the samples. Figure 3 is depicting optical image of sample, hybrid film with small patch are appearing in image. Mapping of 2 D and D + G band show about uniformity of sample.

Table 1. Position of D, G, 2D and D + G peaks in Raman spectra.

Sample	D peak position (cm^{-1})	G peak position (cm^{-1})	2D peak position (cm^{-1})	D + G peak position (cm^{-1})
1	1361.9	1591.8	2728.9	2997
2	1353.2	1582.6	2690.9	2938
3	1343.2	1582.6	2700.1	2938.2

Figure 4 is showing SEM micrograph of sample deposited at different temperatures. It is clear from these figure that density of CNTs is changing with temperature. The benefit of depositing film directly on Ni substrate, without help of nanoparticle is that there is simultaneous growth of CNTs and graphene like film. PECVD is well known deposition method for substrate free growth of graphene. Although graphene like film grown by PECVD shows lack in perfect hexagonal structure due to interaction with high energetical species and plasma, yet grown graphene has promising application in many other field. To confirm presence of graphene like film, TEM was performed. Figure 5 depicting TEM micrographs of sample deposited at 700 °C. Coexistence of both graphene and CNTs is cleared from this Figure 5. Graphene is not in form of single layer.

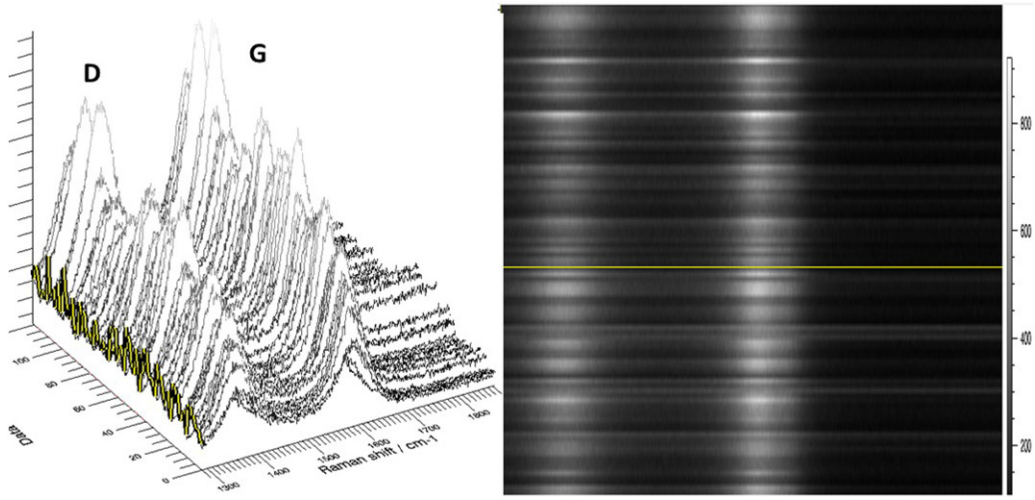

Figure 2. Raman mapping of D and G peaks.

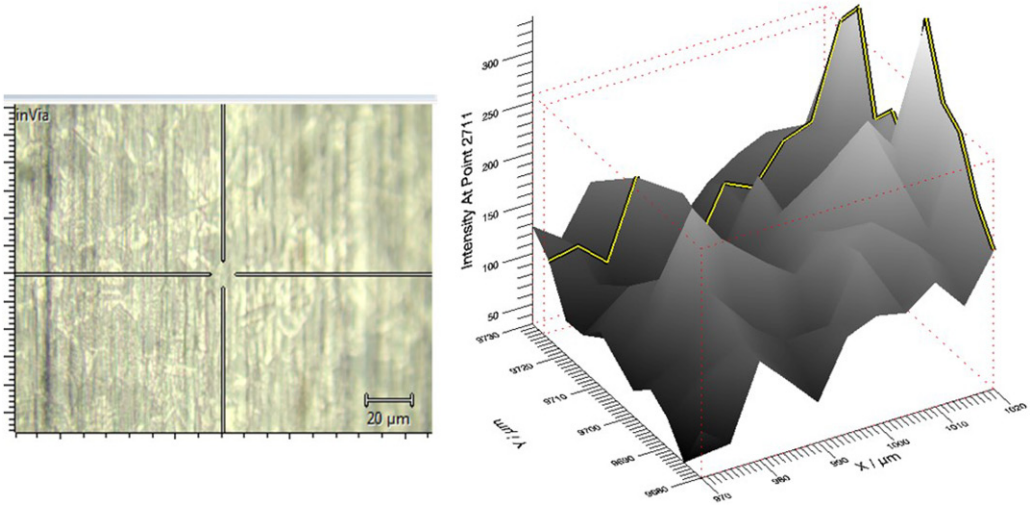

Figure 3. Optical image of Raman mapped sample.

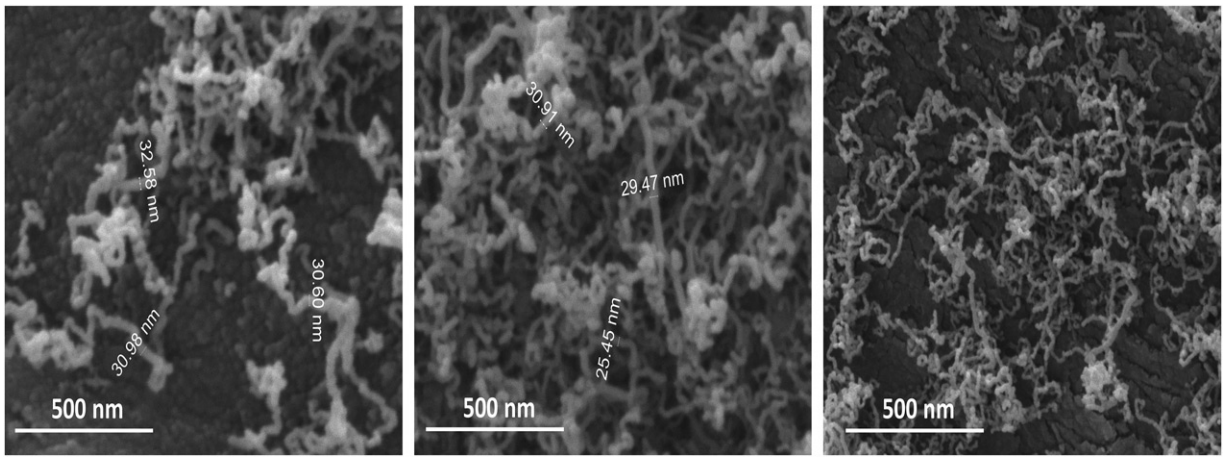

Figure 4. SEM micrograph of CNT-graphene like hybrid film deposited at 500, 600 and 700 °C.

Chokalingam et. al.,[9] have proposed growth model for CNT-graphene like hybrid film. At high temperature there is growth of graphitic nano-island, which act as nucleation center for CNTs growth. At the same time carbon diffuse into Ni, which leads to graphene-like hybrid film after segregation by post fast cooling.

3.2. Wettability property

Microscopic roughness plays an important role for wettability properties of CNTs-graphene-like-hybrid film. There are two models proposed for wettability properties. Wenzel model is applied if the water fill into groves of p protrusions on surface.[14] $cos\,\Theta_a^w = r\ cos\,\Theta$, where Θ_a^w and Θ are

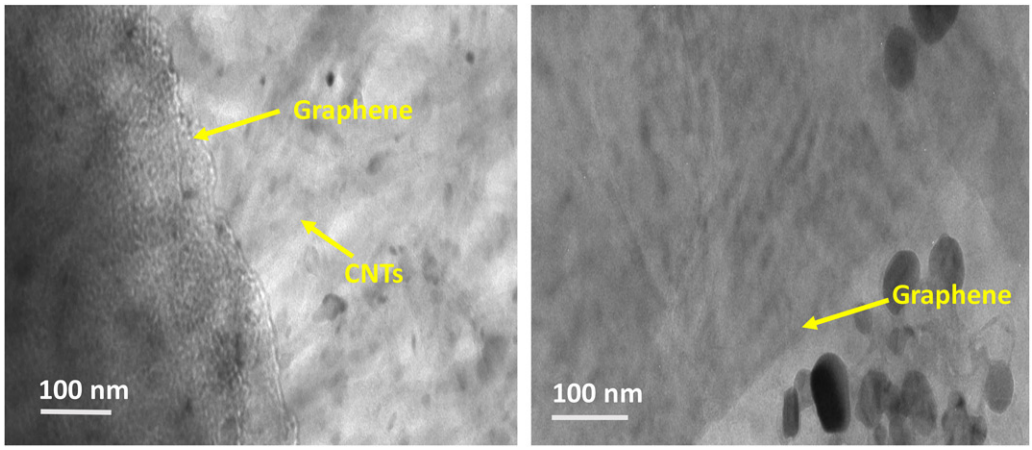

Figure 5. TEM micrograph of CNT-graphene like hybrid film deposited at 600 °C.

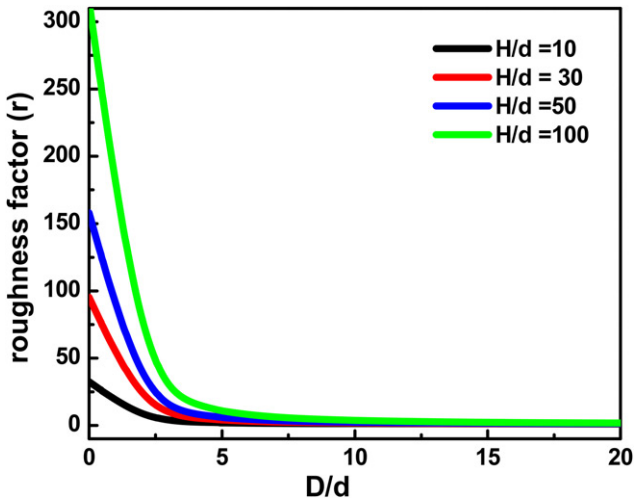

Figure 6. Variation of roughness.

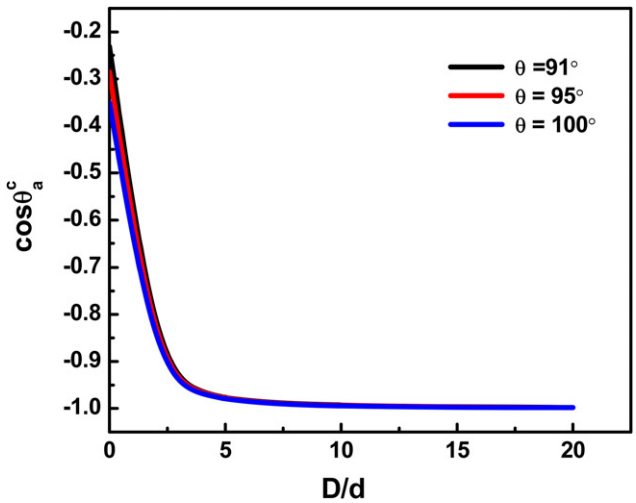

Figure 7. Variation of contact angle.

apparent contact angle on rough surface and ideal contact angle on flat surface, respectively, and the surface roughness factor r is the ratio of actual surface area to the flat area. Cassie–Baxter model[15] can be used if liquid can not penetrate into the grooves of the protrutions on the surface, according to which $cos\,\Theta_a^c = -1 + \Phi_s\ (cos\,\Theta + 1)$, Φ_s being

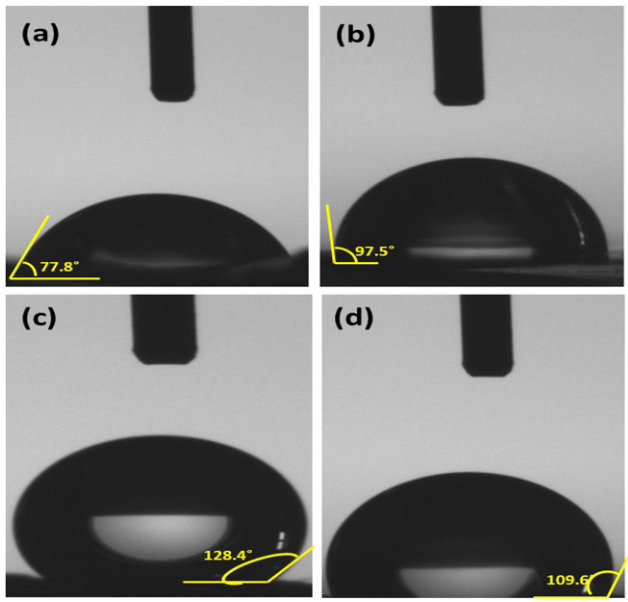

Figure 8. Contact angle measurement to bare nickel and film deposited at different temperature.

the solid fraction on the whole supporting surface. Wang et al.[16] assumed roughness r as

$$r = 1 + \frac{\pi H/d}{(1 + D/d)^2}$$

Where D, H and d are spacing, height, and diameter of the protrutions.

The effect on roughness r as function of D/d with different H/d ration is sown in Figure 6. The value of Θ_a^c with function of D/d is sown in Figure 7. It is clear that the contact angle can be tailored by changing the D/d ratio of CNTs.

Figure 8 shows the contact angle of the bare nickel and hybrid film deposited at 500, 600 and 700 °C. Figure 9 is depicting bar graph representing contact angle with optical image. The bare nickel as contact angle of 77.8°, depicting its hydrophilic nature. After deposition the contact angle has increased to 97.5, 128.4 and 109.6°, showing hydrophobic nature of hybrid film. By measuring the wetting data, we have also measured interaction potential per unit area

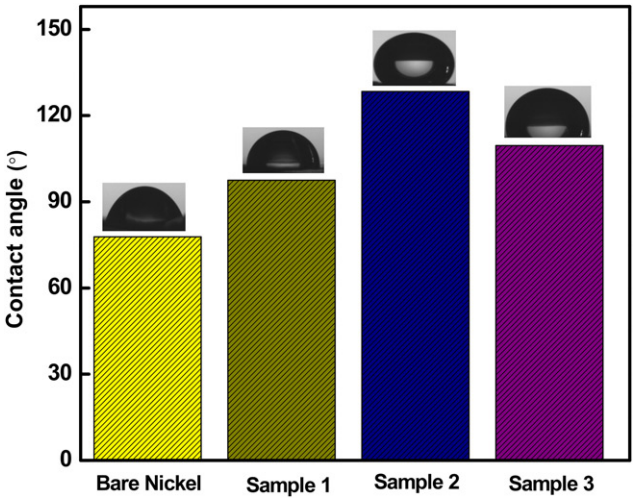

Figure 9. Contact angle for bare Ni and hybrid film deposited at 500, 600 and 700 °C.

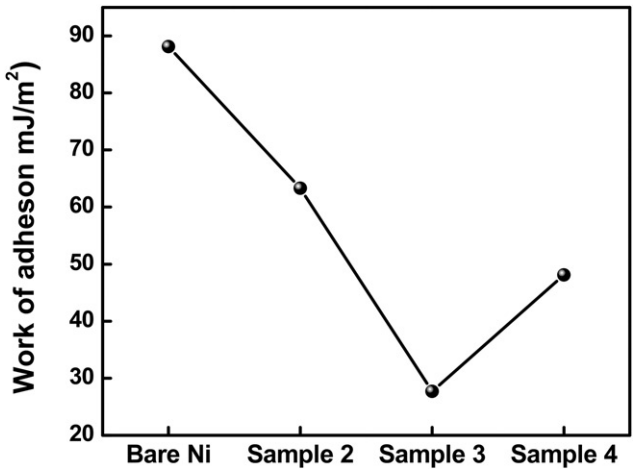

Figure 10. Variation of work of adhesion.

between water and film. Li et. al. have depicted that most of interaction of water is result of graphene, not due to underlying substrate.[17] We have also assumed that the interaction is due to film only.

The wetting parameter work of adhesion W, spreading energy S, wetting tension F and interfacial energy can be calculated from contact angle measurement according to relations:

$$W = \gamma_s + \gamma_l - \gamma_{sl} = \gamma_{lv}(1 + cos\theta)$$

$$S = \gamma_s - (\gamma_l + \gamma_{sl})$$

$$\Delta F = \gamma_s - \gamma_{sl} = \gamma_{sl} cos\theta$$

γ_{lv} is surface tension for water having value 72.8.[18] Work of adhesion W is interlinked to wettability properties. For more adhesion, water must wet substrate adequately. Work of adhesion W, calculated from equation was found to be 88.1, 63.3, 27.7 and 48.1 mJ/m^2 shown in Figure 10. Chi et. al.,[19] have calculated the work of adhesion for individual CNT, Graphene and hybrid film and found the work of adhesion as $0.25\gamma_l$, $1.06\gamma_l$ and $0.71\gamma_l$ for CNT, Graphene and hybrid film, respectively. This indicates work of adhesion is smaller for CNTs compared to Graphene. The variation of work of adhesion may indicate amount of graphene in different samples.

Deshmukh et. al.[18] have found that surface energy for water as probe liquid is given by

$$S.\ E. = 2.9 \times 10^{-5}(\theta)^3 - 0.00652\ (\theta)^2 - 0.1326\ (\theta) + 72.8$$

The surface energy calculated by this relation was calculated and found to be 266.6, 562.2 and 361.7 mJ/m^2 respectively.

4. Conclusion

In summary, we have deposited CNT-graphene-like hybrid film and studied their wetability properties successfully. SEM and TEM micrographs confirming deposition of hybrid CNT-graphene-like hybrid film. As far as we know, this is the first time that the wettability of these single step deposited hybrid CNT-graphene-like hybrid film has been studied. Compare to hydrophobic nature of Ni substrate, wettability properties have been successfully tuned to hydrophobic by these films. Effect of CNTs roughness as also been studied theoretically, showing strongly dependence of wettability properties on diameter, height and interspacing.

References

[1] Feng, L.; Li, S.; Li, Y.; Li, H.; Zhang, L.; Zhai, J.; Song, Y.; Liu, B.; Jiang, L.; Zhu, D. Super-Hydrophobic Surfaces: From Natural to Artificial. *Adv. Mater.* **2002**, *14*, 1857–1860.

[2] Meng, L. Y.; Park, S. J. Superhydrophobic Carbon-Based Materials: A Review of Synthesis, Structure, and Applications. *Carbon Lett.* **2014**, *15*, 89–104. DOI: 10.5714/CL.2014.15.2.089.

[3] Zheng, L.; Li, Z.; Bourdo, S.; Khedir, K. R.; Asar, M. P.; Ryerson, C. C.; Biris, A. S. Exceptional Superhydrophobicity and Low Velocity Impact Icephobicity of Acetone-Functionalized Carbon Nanotube Films. *Langmuir* **2011**, *27*, 9936–9943. DOI: 10.1021/la201548k.

[4] Chen, Z.; Dong, L.; Yang, D.; Lu, H. Superhydrophobic Graphene-Based Materials: Surface Construction and Functional Applications. *Adv. Mater.* **2013**, *25*, 5352. DOI: 10.1002/adma.201302804.

[5] Lee, C. H.; Johnson, N.; Drelich, J.; Yap, Y. K. The Performance of Superhydrophobic and Super Oleophilic Carbon Nanotube Meshes in Water–Oil Filtration. *Carbon* **2011**, *49*, 669–676. DOI: 10.1016/j.carbon.2010.10.016.

[6] Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Graphene-Based Composite Material. *Nature* **2006**, *442*, 282–286. DOI: 10.1038/nature04969.

[7] Shin, Y. J.; Wang, Y. Y.; Huang, H.; Kalon, G.; Wee, A. T. S.; Shen, Z. X.; Bhatia, C. S.; Yang, H. Surface-Energy Engineering of Graphene. *Langmuir* **2010**, *26*, 3798–3802. DOI: 10.1021/la100231u.

[8] Wang, S. R.; Zhang, Y.; Abidi, N.; Cabrales, L. Wettability and Surface Free Energy of Graphene Films. *Langmuir* **2009**, *25*, 11078. DOI: 10.1021/la901402f.

[9] Chokalingam, S.; Bisht, A.; Panwar, O. S.; Kesarwani, A. K.; Singh, B. P.; Chand, J.; Singh, V. N. Synthesis, Structural and Field Emission Properties of Multiwall Carbon Nanotube-Graphene-like Nanocarbon Hybrid Films Grown by Microwave Plasma Enhanced Chemical Vapor Deposition. *Mater. Chem. Phys.* **2015**, *156*, 38–46. DOI: 10.1016/j.matchemphys.2015.02.016.

[10] DiLeo, R. A.; Landi, B. J.; Raffaelle, R. P. Purity Assessment of Multiwalled Carbon Nanotubes by Raman Spectroscopy. *J. Appl. Phys.* **2007**, *101*, 064307. DOI: 10.1063/1.2712152.

[11] Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Raman Spectrum of Graphene and Graphene Layers. *Phys. Rev. Lett.* **2006**, *97*, 1874013. DOI: 10.1103/PhysRevLett.97.187401.

[12] Tan, P. H.; Deng, Y. M.; Zhao, Q. Temperature-Dependent Raman Spectra and Anomalous Raman Phenomenon of Highly Oriented Pyrolytic Graphite. *Phys. Rev. B* **1998**, *58*, 5435–5439. DOI: 10.1103/PhysRevB.58.5435.

[13] Pimenta, M. S.; A.; Dresselhau, G. M. S.; Dresselhaus, Canc, L. G.; Ado, Jorio, A.; Saito, R. Studying Disorder in Graphite-Based Systems by Raman Spectroscopy. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1276–1291. DOI: 10.1039/B613962K.

[14] Wenzel, R. N. Resistance of Solid Surfaces to Wetting by Water. *Ind. Eng. Chem.* **1936**, *28*, 988–994. DOI: 10.1021/ie50320a024.

[15] Cassie, A. B. D.; Baxter, S. Wettability of Porous Surface. *Trans. Faraday Soc.* **1944**, *40*, 546–551. DOI: 10.1039/tf9444000546.

[16] Wang, H. Z.; Huang, Z. P.; Cai, Q. J.; Kulkarni, K.; Chen, C.-L.; Carnahan, D.; Ren, Z. F. Reversible Transformation of Hydrophobicity and Hydrophilicity of Aligned Carbon Nanotube Arrays and Buck Papers by Dry Processes. *Carbon* **2010**, *48*, 868–875. DOI: 10.1016/j.carbon.2009.10.041.

[17] Li, Z.; Wang, Y.; Kozbial, A.; Shenoy, G.; Zhou, F.; McGinley, R.; Ireland, P.; Morganstein, B.; Kunkel, A.; Surwade, S. P.; et al. Effect of Airborne Contaminants on the Wettability of Supported Graphene and graphite. *Nat. Mater.* **2013**, *12*, 925–931. DOI: 10.1038/nmat3709.

[18] Deshmukh, M.; Kalim, Khatake, S. M.; Joshi, G. Surface Properties of Graphene Oxide Reinforced Polyvinyl Chloride Nanocomposites. *J Polym. Res.* **2013**, *20*, 286.

[19] Chi, X.; Zhang, J.; Nshimiyimana, J. P.; Hu, X.; Pei, W.; Liu, S.; Liu, J.; Chu, W.; Sun, L. Wettability of Monolayer Graphene/Single-Walled Carbon Nanotube Hybrid Films. *RSC Adv.* **2017**, *7*, 48184–48188.