Appl Nanosci (2017) 7:125–129
DOI 10.1007/s13204-017-0549-z

ORIGINAL ARTICLE

A new approach for orientation-controlled growth of CNTs: an in-depth analysis on the role of oxygen plasma treatment to catalyst

Nishant Tripathi[1] · **S. S. Islam**[1]

Received: 3 February 2017 / Accepted: 9 February 2017 / Published online: 20 February 2017
© The Author(s) 2017. This article is published with open access at Springerlink.com

Abstract In this paper, a novel and easy technique is proposed for orientation controlled growth of MWNTs. The results indicate that when CNT growth was carried over the substrate, not treated with plasma, horizontal network of MWNTs was formed. Plasma treatment to the substrate prior to CNTs growth led to formation of vertically aligned MWNTs. An in situ growth as a function of plasma treatment time reveals the mechanism behind this flip process. All experiments were performed under atmospheric pressure. At every step during time-dependent growth process, CNTs were characterized using FESEM, HRTEM, and Raman spectroscopy. Iron sputtered silicon substrate was also investigated to validate the excellent formation of as-grown vertical CNTs and also to analyze the role of oxygen plasma behind the orientation-controlled growth. The as-grown CNTs over the iron sputtered silicon substrate with or without plasma treatment were characterized by FESEM and AFM. The successful orientation-controlled growth of CNTs was achieved.

Keywords Vertically aligned MWNTs · Plasma treatment · Growth mechanism

✉ S. S. Islam
sislam@jmi.ac.in

1 Centre for Nanoscience and Nanotechnology, Jamia Millia Islamia (A Central University), Jamia Nagar, New Delhi 110025, India

Introduction

Invention of CNTs triggers a new era of science and worldwide, researchers have started working on development of new nanomaterials and application based upon invented nanomaterials (Sharma et al. 2016; Singh et al. 2017; Sharma and Gupta 2016). Among all nanomaterials, due to high carrier mobility, good stability, and tunable band-gap structure with small diameter, CNTs become a perfect structure for making channel for high-performance field effect transistors (FETs), integrated circuits, and other electronic applications (Zhang et al. 2016) and hence, research communities have started focusing on various application aspects of CNTs. The requirement of structural quality of CNTs is different for different types of applications. The researchers can tune the structural quality of CNTs as per the requirement, either by synthesizing the CNTs in bulk and later tuning morphology of CNTs or by tuning the CNT parameters at the time of synthesis. To eliminate post-synthesis manipulation or assembly to make CNTs useful for application purposes, we have already discussed in detail in previous papers about controlling various parameters like morphology, structure, and dimensions of CNTs during growth process (Tripathi et al. 2014a, b, c, 2015a, b, c). However, analysis of an important parameter, i.e. orientation of CNTs is still required to achieve perfect structure of CNTs. It is important due to requirement of different types of orientation for different applications. For example, horizontally aligned network of CNTs is suitable for fabricating gas sensor (Guerin et al. 2012; Lim et al. 2012; Poche et al. 2013), while vertically aligned network of CNTs is suitable for field emission (Cui et al. 2015; Lin et al. 2015). In order to fulfil this requirement, the researchers control the orientation of CNTs by applying magnetic and electric field (Lee et al.

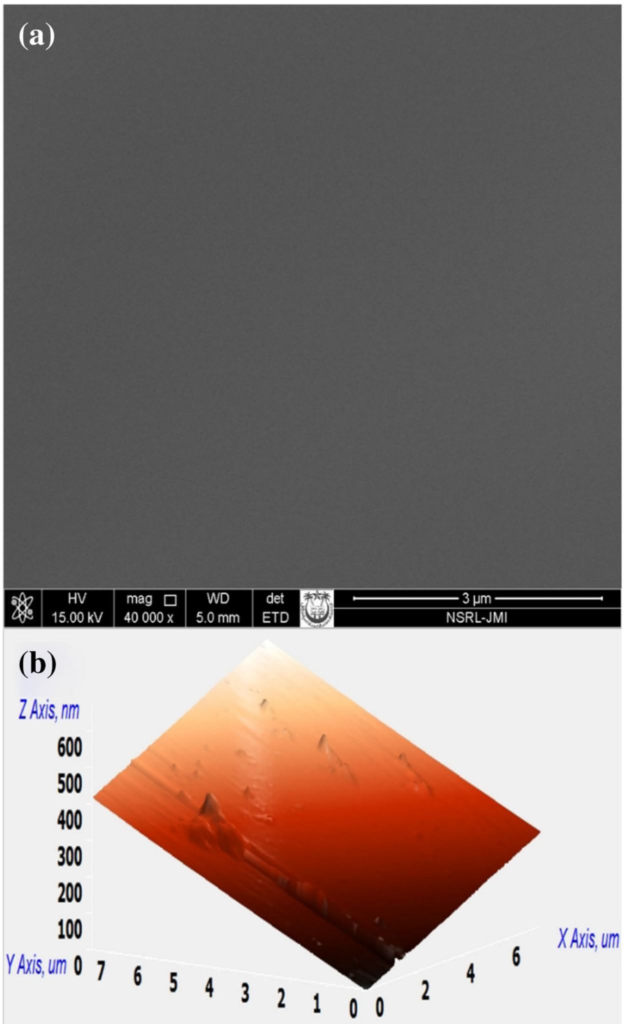

Fig. 1 FESEM and AFM images of sputtered sample prior to CNT growth

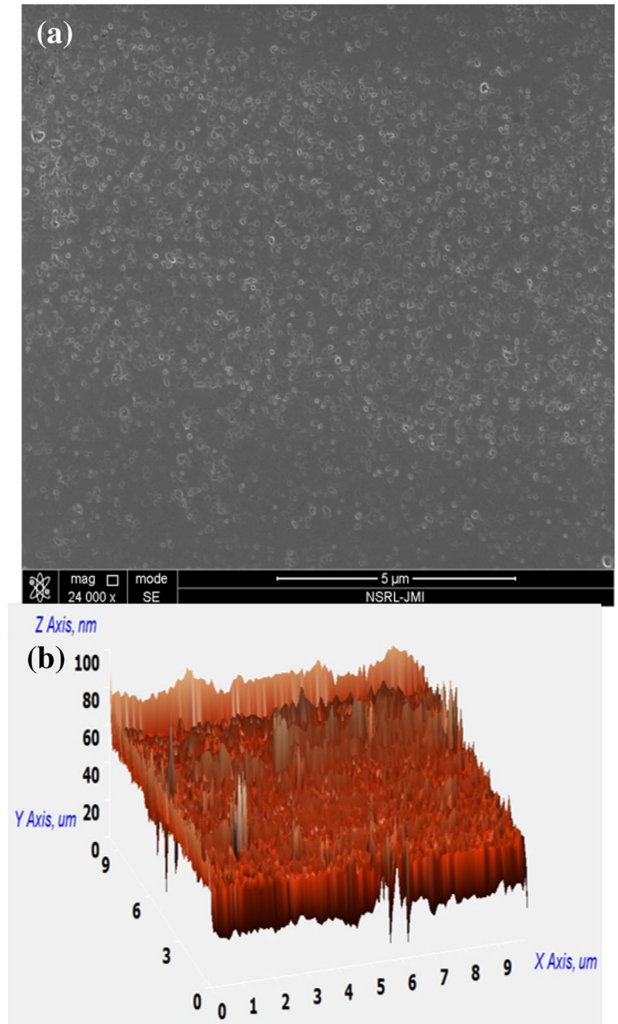

Fig. 2 FESEM and AFM images of oxygen-plasma-treated iron-sputtered silicon

2003; Ko and Tsukruk 2006) on substrate during growth process of CNTs. Su et al. also carried out research on the orientation of CNTs and controlled it using crystalline surface (Su et al. 2000) as well as performing CNT growth process on porous silicon substrate (Veca et al. 2012). But, so far, reported techniques for controlling the orientation of grown CNTs are very tough and complex and sometimes also damage the CNT structure (Kim et al. 2005).

In the present paper, we report a relatively simple technique to control the orientation of as-grown CNTs. In this technique catalyst-sputtered substrate was treated with oxygen plasma. The substrate as treated with oxygen plasma was then loaded to CVD and usual CNT growth process was run. As a result, vertically oriented CNTs were achieved. On the other hand, horizontally oriented CNTs were formed on the substrate which was not treated by oxygen plasma. A detailed discussion on The role of oxygen plasma treatment on iron thin film and its outcomes on CNT growth are discussed in detail in the next sections.

Experiment

A thin layer of 2 nm iron catalyst was deposited on 5 × 5 mm P-type silicon (100) substrate by RF-sputtering technique. The sputtered sample was cleaned by ultrasonicator in IPA for 5 min. The process flow of CNTs growth involved Placement of cleaned substrate in CVD system, and growth was carried out at temperature ramp of 500 °C/h under environment of 60 sccm Ar as carrier gas. When temperature of CVD chamber reached 800 °C, C_2H_2 gas was flown into the chamber with a flow rate of 20 sccm. After 10 min, C_2H_2 gas flow was stopped and the heater of CVD system was switched off; and the chamber of CVD system was allowed to cool down to room temperature in the presence of Argon. After cooling, the sample was taken

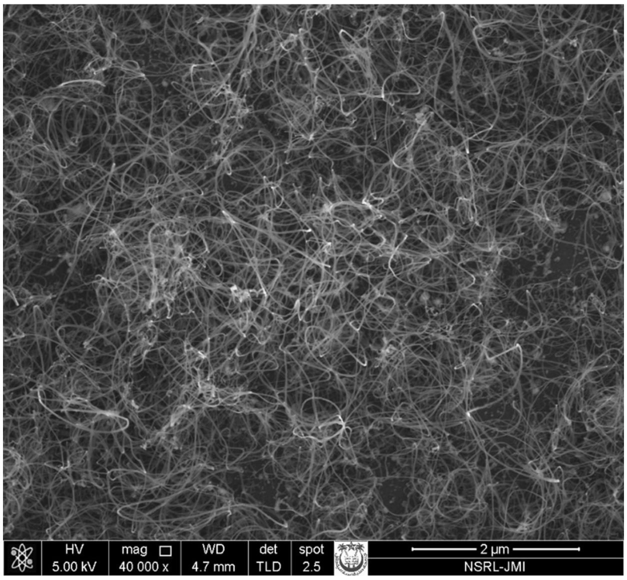

Fig. 3 FESEM images of horizontal network type CNTs

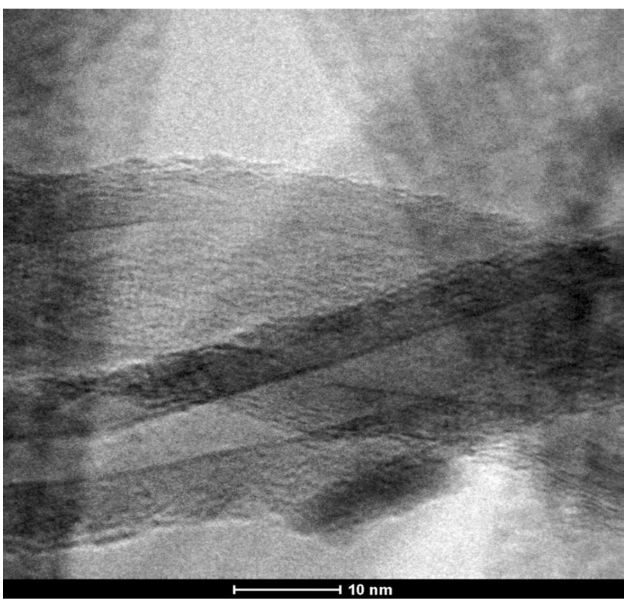

Fig. 4 HRTEM image of grown CNTs without plasma treatment

out. To study the effect of oxygen plasma treatment, the catalyst-coated substrate was treated with oxygen plasma treatment for 10 min. The plasma-treated substrate was then loaded into the chamber of CVD system and CNT growth process was carried out in the same way as discussed before.

The surface morphology of as-grown samples was characterized by FESEM (NOVA NANO SEM 450, FEI) and the structural quality of CNTs was studied with Micro-Raman spectrometer with 488 nm Ar^+ laser (LabRAM HR800, JY) and HRTEM (Technai, 300 kV, F30,

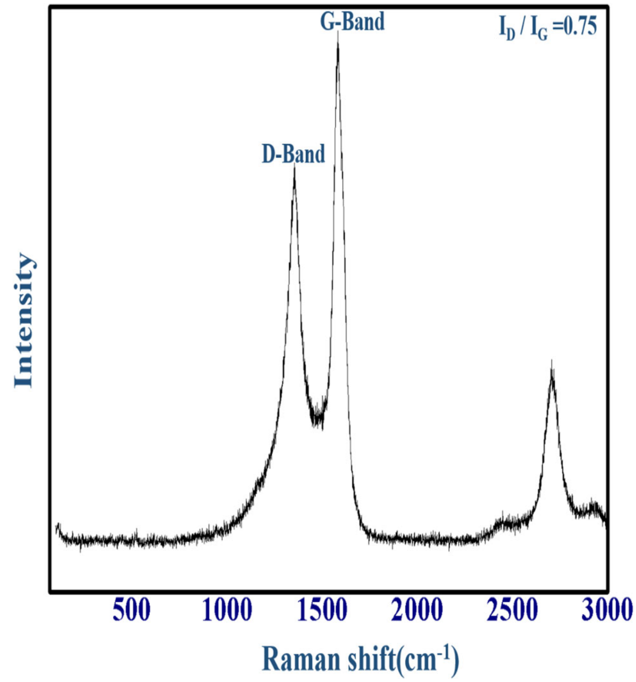

Fig. 5 Raman spectra of grown CNTs without plasma treatment

G^2Stwin). The effect of oxygen plasma of the structure of catalyst was also studied using FESEM and AFM.

Results and discussion

Figure 1 shows the FESEM and AFM images of iron-sputtered silicon sample. From these images, it is clear that the surface of as-sputtered silicon substrate has negligible surface roughness. When sputtered silicon substrate was treated with oxygen plasma, the surface roughness increases (Fig. 2). Figure 3 shows the FESEM image of CNTs grown on as-sputtered (without plasma treatment) substrate which shows dense horizontal network of CNTs. Figure 4 shows the HRTEM image for same CNTs' grown sample. It shows grown CNTs have 10–12 nm diameter distribution. To verify the structural quality, CNTs' grown samples were also investigated by Raman spectroscopy (see Fig. 5). It shows characteristic G-band and D-band with I_D/I_G ratio 0.6, which verify the good structural quality of grown CNTs.

Figure 6 shows the FESEM image of CNTs grown on oxygen-plasma-treated substrate, and it was observed that ultra-dense carpet of vertically aligned CNTs was grown on this substrate. It is already reported that oxygen plasma treatment makes the surface rough and also creates defects on the surface (Poche et al. 2013). This is verified by AFM and FESEM images of Fig. 2. These defects and roughness provide extra nucleation sites for attachment of carbon for CNT growth.

Figure 7, shows the proposed growth mechanism for horizontal network. In case of horizontal network,

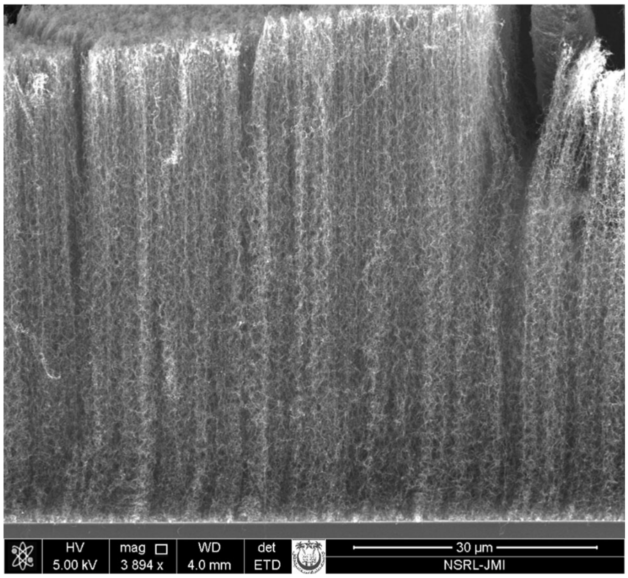

Fig. 6 FESEM images of grown CNTs in plasma treated catalyst

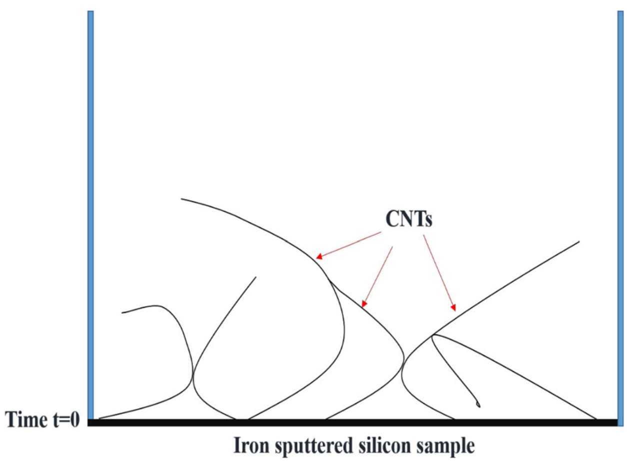

Fig. 7 Side view for growth mechanism for horizontal network type CNT growth

nucleation sites are far from each other. When CNT growth initiates, the newly coming carbon atoms apply a downward force on nucleated CNTs. This force tends to bend CNTs just after the growth is started. And due to low nucleation sites, nucleated CNTs continue to grow in bending direction without colliding with other grown CNTs. On the other hand, plasma treatment sample is rich in nucleation sites, so large number of CNTs nucleate at a time. So, when a nucleated CNT bends due to force exerted by the incoming carbon atoms, it collides with other growing CNTs and its growth direction changes (see Fig. 8). Successive collisions, one after the other (see W, X, Y and Z in plot of Fig. 8), do not allow these CNTs to bend. As a result, the CNTs are grown in vertical direction. Figures 9 and 10 show the HRTEM and Raman spectra

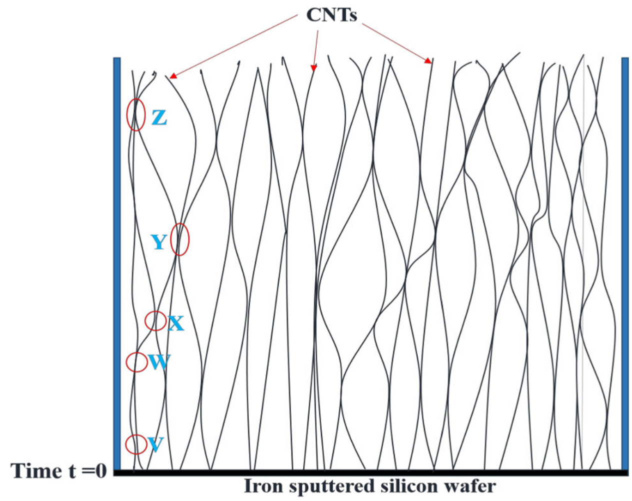

Fig. 8 Side view for growth mechanism for vertically aligned type of CNT growth

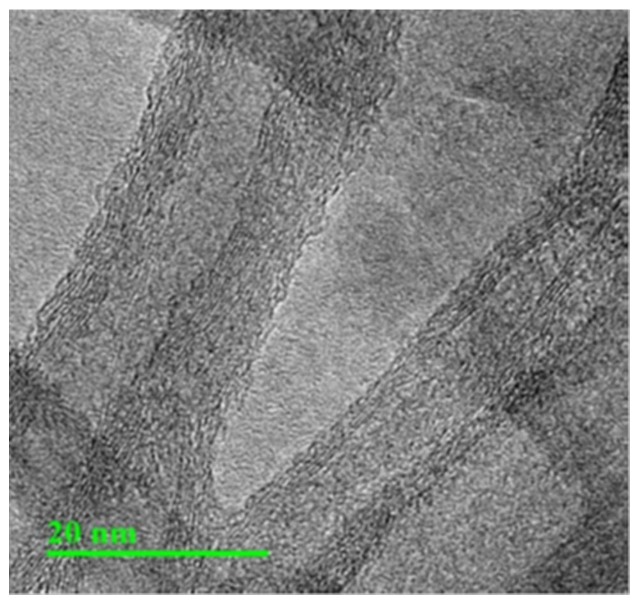

Fig. 9 HRTEM micrograph for vertically aligned CNT growth

images of vertically aligned CNTs, in which we observe better quality of CNTs which are grown on oxygen-plasma-treated sample. The diameter of grown CNTs is observed around 4–8 nm with lesser I_D/I_G ratio. Better structural quality and lesser diameter have been due to perfect balance between production and deposition of carbon atoms.

Conclusion

It is concluded that oxygen plasma treatment, an easy prior growth step, can change the orientation of CNTs. CNT growth process without plasma treatment results in

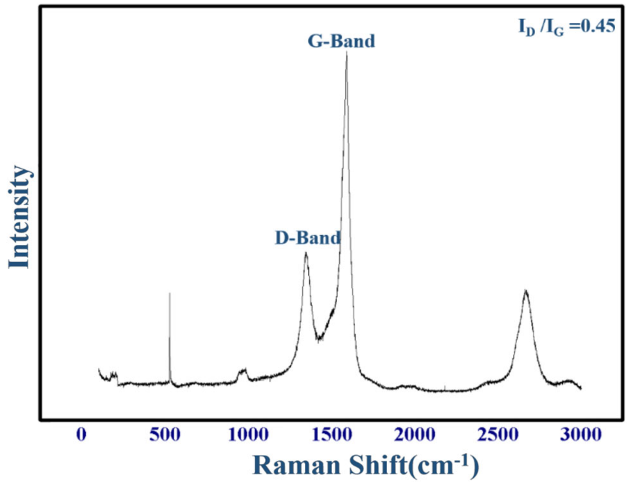

Fig. 10 Raman spectra for vertically aligned CNT growth

horizontal network and the same growth process without prior oxygen plasma treatment results in dense carpet of vertically aligned CNTs. The growth mechanism behind the attracting results was explained. In summary, the orientation as well as yield of CNTs was successfully tuned by using simpler techniques.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

Cui L, Chen J, Yang B, Jiao T (2015) High current emission from patterned aligned carbon nanotubes fabricated by plasma-enhanced chemical vapor deposition. Nanoscale Res Lett 10:483. doi:10.1186/s11671-015-1192-9

Guerin H, Tsamados D, Poche HL, Dijon J, Ionescu AM (2012) In-situ grown horizontal carbon nanotube membrane. Microelectron Eng 97:166–168. doi:10.1016/j.mee.2012.05.017

Kim SH, Na SW, Lee NE, Nam YW, Kim YH (2005) Effect of surface roughness on the adhesion properties of Cu/Cr films on polyimide substrate treated by inductively coupled oxygen plasma. Surf Coat Technol 200:2072–2079. doi:10.1016/j.surfcoat.2005.05.021

Ko H, Tsukruk VV (2006) Liquid-crystalline processing of highly oriented carbon nanotube arrays for thin-film transistors. Nano Lett 6(1443):1448. doi:10.1063/1.1535269

Lee KH, Cho JM, Sigmund W (2003) Control of growth orientation for carbon nanotubes. Appl Phys Lett 82:448–450. doi:10.1063/1.1535269

Lim JH, Mulchandani A, Myung NV (2012) Single-walled carbon nanotubes based chemicapacitive sensors. J Nanosci Nanotechnol 12:1517–1520. doi:10.1166/jnn.2012.4605

Lin PH, Sie CL, Chen CA, Chang HC, Shih YT, Chang HY, Su WJ, Lee KY (2015) Field emission characteristics of the structure of vertically aligned carbon nanotube bundles. Nanoscale Res Lett 10:1–6. doi:10.1186/s11671-015-1005-1

Poche HL, Guerin H, Pohle R, Bolaños MF, Dijon J, Ionescu AM (2013) Resistive gas sensors fabricated by wafer-scale, in situ integration of horizontal carbon nanotube membranes. Transducers 006:2584–2587. doi:10.1109/Transducers.2013.6627334

Sharma P, Gupta N (2016) Model for threshold voltage instability in top-gated nanocrystalline silicon thin film transistor. J Comput Electron 15:666–671. doi:10.1007/s10825-015-0789-7

Sharma P, Tripathi N, Gupta N (2016) Nanocrystalline silicon thin film prepared by e-beam evaporation for display application. J Mater Sci. doi:10.1007/s10854-016-6002-3

Singh J, Sahu K, Kuriakose S, Tripathi N, Avasthi DK, Mohapatra S (2017) Synthesis of nanostructured TiO2 thin films with highly enhanced photocatalytic activity by atom beam sputtering. Adv Mater Lett 8:107–113. doi:10.5185/amlett.2017.6432

Su M, Li Y, Maynor B, Buldum A, Lu JP, Liu J (2000) Lattice-oriented growth of single-walled carbon nanotubes. J Phys Chem B 104:6505–6508. doi:10.1021/jp0012404

Tripathi N, Mishra P, Joshi B, Harsh Islam SS (2014a) Catalyst free, excellent quality and narrow diameter of CNT growth on Al_2O_3 by a thermal CVD technique. Physica E 62(43):47. doi:10.1016/j.physe.2014.04.011

Tripathi N, Mishra P, Islam SS (2014) Effect of growth temperature on the diameter distribution and yield of carbon nanotubes. In: Physics of semiconductor devices, environmental science and engineering, Springer, Cham, pp 645–646. doi: 10.1007/978-3-319-03002-9_164

Tripathi N, Mishra P, Joshi B, Islam SS (2014c) A systematic study on growth of CNTs with liquid chemical salts as catalysts: a fine control on orientation of CNTs. Adv sci lett 20:1612–1615. doi:10.1166/asl.2014.5554

Tripathi N, Mishra P, Harsh H, Islam SS (2015a) Fine-tuning control on CNT diameter distribution, length and density using thermal CVD growth at atmospheric pressure: an in-depth analysis on the role of flow rate and flow duration of acetylene (C_2H_2) gas. Appl Nanosci 5:19–28. doi:10.1007/s13204-013-0288-8

Tripathi N, Mishra P, Joshi B, Islam SS (2015b) Precise control over physical characteristics of carbon nanotubes by differential variation of argon flow rate during chemical vapor deposition processing: a systematic study on growth kinetics. Mater Sci Semicond Process 35:207–215. doi:10.1016/j.mssp.2015.03.014

Tripathi N, Moinuddin MG, Islam SS (2015c) Growth of SWNTs using Cu (NO3) 2 and CuO a systematic study on role of oxygen in growth of CNTs. INDICON, IEEE 1:3. doi:10.1109/INDICON.2015.7443847

Veca LM, Craciunoiu F, Kusko M, Danila M, Dinescu A (2012) Porous silicon decorated metallic nanoparticles for growing vertically aligned carbon nanotube. IEEE. doi:10.1109/SMICND.2012.6400692

Zhang F, Hou PX, Liu C, Wang BW, Jiang H, Chen ML, Sun DM, Li JC, Cong HT, Kauppinen EI, Cheng HM (2016) Growth of semiconducting single-wall carbon nanotubes with a narrow band-gap distribution. Nat Commun 7:1–7. doi:10.1038/ncomms11160