Research Article

One Step Fabrication of Aligned Carbon Nanotube Sheet via FC-CVD Technique

Manoj Sehrawat, Mamta Rani, and Bhanu Pratap Singh

1Advanced Carbon Products and Metrology, CSIR-National Physical Laboratory, New Delhi 110 012, India
2Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201 002, India

Correspondence should be addressed to Bhanu Pratap Singh; bps@nplindia.org

Received 10 May 2022; Revised 17 June 2022; Accepted 29 June 2022; Published 16 July 2022

The rising need for lightweight and strong mechanical structures has contributed significantly towards the development of CNT macrostructures; however, the interplay of parameters and their discontinuous synthesis have obstructed their delivery to commercial level. Herein, floating catalyst chemical vapor deposition technique (FC-CVD) has been employed for the fabrication of 90 cm long CNT sheet via continuous production of CNT aerogel. High degree of graphitization, thermal stability and purity have been indicated by Raman spectroscopy ($I_d/I_g = 10.03$), thermogravimetric analysis, and SEM studies. Continuous winding of CNT aerogel has increased the alignment into the sample which resulted into high electrical conductivity value of 21400 S/m. Furthermore, the alignment has been quantified by calculating optical anisotropic ratio $I_d/\perp$ and conductivity anisotropic ratio $\kappa/\perp$ which were calculated to be 4.63 and 3.4, respectively, and show reasonable agreement. These findings indicate that a well correlation of synthesis parameters results in highly aligned CNT sheet structure in a single step.

1. Introduction

In search of increased performance and functionality, Iijima led to the discovery of carbon nanotube (CNT) in 1991 [1], which are reported to possess exceptionally high mechanical, thermal, and electrical properties with very low density [2–5]. These hollow tubes of graphene are solely made up of hexagonal rings of $sp^2$ bonded carbon atoms which imparts unique atomistic feature [6]. Even after three decades of their introduction to the scientific world, their continuous synthesis of aligned and densely stacked CNT structure for bulk production still lacks an efficient and reliable method. Chemical vapor deposition (CVD) which is a low temperature synthesis process has overtaken the previously opted laser ablation and arc discharge method which suffered from high energy consumption due to high temperature requirement [7].

Indirect preparation of CNT sheet via vacuum filtration [8], solution spraying [9], hydroentangling [10], electrochemical deposition [11], domino pushing [12], and dry-drawing techniques [13] includes intermediate steps and produces random alignment. Sooner, substrate-based CVD process introduced the concept of vertically aligned spinnable CNT forest which were used for preparation of CNT macroassemblies such as yarn and sheet via domino pushing [12] and dry-drawing techniques [13]; however, this method is suitable for laboratory scale only [14, 15]. Among other explorations, floating catalyst chemical vapor deposition (FCCVD) technique has been found the most promising of all, due to its easy scalability, appreciable yield, purity, and easy maneuverability of parameters [16, 17]. In this technique, the synthesis of CNTs occurs in floating gaseous environment leading to formation of aerogel, which is being continuously collected in the form of sheet (in this study), yarn, and ribbon [18]. However, the multidimensionality and interdependence of parameters which includes synthesis temperature, precursor nature, their relative concentrations and injection rate, deposits on reactor wall, gaseous medium, and flow rate of carrier gases have made conclusions difficult for this reaction [6, 19].
This technique offers a cost-effective route to assemble nanomaterials into macroscopic form such as sheet, yarn, and ribbon and thus has motivated researchers to grasp a clear understanding of it. Various reported studies have used different organic precursors such as methane, toluene, benzene, acetone, ethanol, and butanol [20–24]; however, carbon sources with oxygen functionalities are found to favor the synthesis process by eliminating amorphous impurities [25]. Cheng et al. have correlated the concentration of thiophene used with the average diameter and morphology of produced CNTs [26]. Supply rate of both carrier gases and precursors has direct impact on the diameter of nanotubes. Higher injection rate of fuel induces more collisions between the catalyst particles, thus favoring larger diameter CNTs. Conversely, higher gas flow rates reduces the residence time of nanoparticles increasing their mean free path, thus producing low diameter CNTs [27, 28].

CNT material thus produced offers properties such as high ampicities, appreciable mechanical strength, and high thermal conductivity which can open up its wide application in textile sector [29, 30]. Reports have shown the excellent fire retardant capabilities of CNT sheets for use in protective equipment of firefighters [31]. Hu et al. have investigated the promising potential of thin CNT sheet for use in wearable electronics and energy storage devices [32]. Chauhan et al. have explored the postprocessing methods which included densifying and stretching which saw significant improvement in mechanical and electrical performances. These samples were then integrated into composite laminates to enhance the in-plane electrical conductivity and interlaminar shear strength laminated composites [33].

Realizing its immense positivity, preparation of aligned CNT sheet at large scale is highly desirable. Feng et al. [34] reported one step fabrication of free standing high-quality DWCNT film of length 20 cm and width of 0.6 cm only. Liu et al. successfully prepared multilayered sheet of randomly oriented CNTs having dimension of 25 × 20 cm. Furthermore, the density and alignment were improved via poststretching and pressing [35]. Tran et al. continuously spun CNT aerogel at winding rate of 25 m/min in form of CNT film having random arrangement of nanotubes with low crystallinity. Their alignment and packing were further enhanced however by mechanical densification process [36]. Han et al. wounded well-aligned CNT ribbons employing higher gas flow and winding rates, which were densified into film using ethanol spray solution. The synthesized film shows much lower electrical conductivity when compared to ribbon which were attributed to low density and high contact resistance due to presences of gaps in structures [22]. Luo et al. prepared CNT film of controlled size following the principle of layer by layer deposition and condensation of CNT cylinder on ethanol wetted paper strip. Employing this technique, they successfully prepared 50-meter CNT film with width of 1.8 cm [37]. Since the winding process does not involve any stretching, the nanotube network does not show any signs of alignment. Chitranshi et al. prepared CNTH sheet by carefully tuning the process so as to minimize the use of gases (2500 sccm) along with continuous wrapping of material [38]. A detailed state-of-the-art of CNT sheet synthesis has been summarized in Table 1.

A major problem encountered towards the synthesis of CNT sheet is discontinuity of CNT; therefore, we employed larger diameter ceramic reactor [39] in this study to address occasional breaking of sock. Through this strategy, we synthesized 90 cm long continuous CNT sheet by depositing CNT aerogel for a longer period of time at defined parameters. The synthesized CNT sheets have been found to be highly crystalline, stable, and electrically conducting. Moreover, the final produce show appreciable degree of alignment as evidenced by polarized Raman spectroscopy, SEM analysis, and conductivity measurements.

2. Materials and Methods

2.1. Synthesis of Carbon Nanotube Sheet (CNT Sheet). Continuous synthesis of CNT aerogel has been carried out via a horizontal FC-CVD process in which ethanol served a source of carbon, ferrocene facilitated iron atoms which provide surface for CNT synthesis, and thiophene was used as a promoter in this process. The precursor solution containing above three elements were injected at 15 ml/hr using a syringe pump. One end of alumina reactor was kept in one zone furnace set at temperature of 1350°C. The other end of alumina tube was opened in a closed chamber named collection chamber, which has rotating spindle. The complete assembly was flushed initially with argon at 1500 sccm for 10 minutes to check for any potential leakage and make the environment inert. Sooner, the hydrogen was also introduced as carrier gas inside the reactor for delivery of the reactants to the heating zone at flow rate of 700 sccm. The collection chamber has also been continuously flushed with argon during the synthesis process for proper disposal and dilution of hydrogen generated from reactor. The translucent CNT cylinder formed inside the reactor pulled out using a metal rod and attached to a rotating spindle, covered with aluminium foil resulting in formation of CNT sheet. The above process can be seen in Figure 1 which was recorded during the synthesis of sheet. The collection process was done for 15 minutes to ensure the formation of structurally cohesive framework with appreciable thickness after which the supply of reagents was halted and system was cooled under argon atmosphere. The sheet was later detached from the foil and used for various studies.

2.2. Characterization. The produced CNT sheet has been characterized using Renishaw in via Reflex Raman spectroscopic system at laser of wavelength 785 nm. The ratio of intensity of graphitic peak to defect peak has been assessed as a scale of purity for CNT. Polarized Raman study has been performed using a Jobin Yvon T64000 triple Raman spectrometer as laser wavelength of 532 nm to evaluate the degree of alignment in the sample sheet. The incident beam is polarized in directions parallel and perpendicular to CNT sheet alignment, and ratio of the intensities of G-band in respective directions gives a measure of alignment degree in sample. Scanning electron microscope images have been recorded using FE-SEM instrument to visualize the morphology, degree of alignment, and purity of synthesized nanotubes. Thermal studies of the sample have been
<table>
<thead>
<tr>
<th>S. no.</th>
<th>Reactor dimensions (I.D. × length)</th>
<th>Precursors</th>
<th>Precursor flow rate</th>
<th>Gas flow rate</th>
<th>Temperature (°C)</th>
<th>Dimension of film</th>
<th>Alignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>45 × 1800 mm</td>
<td>Xylene (Fe:S 10:1)</td>
<td>9 ml/hr</td>
<td>Ar: 2500-3500 sccm H₂: 500 sccm</td>
<td>1100</td>
<td>10 × 10 cm, thickness 10-80 nm</td>
<td>Random</td>
<td>[40]</td>
</tr>
<tr>
<td>2</td>
<td>65 × 1600 mm</td>
<td>Acetone 3.1 wt%, Fe 0.5 wt% S</td>
<td>12-20 ml/hr</td>
<td>Ar: 100-1000 sccm</td>
<td>1100-1170</td>
<td>20 × 0.6 cm</td>
<td>Random</td>
<td>[34]</td>
</tr>
<tr>
<td>4.</td>
<td>—</td>
<td>Ethanol, Fe (2.0 wt%), S (1.5 wt%)</td>
<td>9 ml/hr</td>
<td>Ar: 2000 sccm H₂: 2000 sccm</td>
<td>1300</td>
<td>25 × 20 cm</td>
<td>Random</td>
<td>[22]</td>
</tr>
<tr>
<td>5</td>
<td>—</td>
<td>Ethanol, ferrocene, thiophene</td>
<td>9 ml/hr</td>
<td>Ar: 2000 sccm H₂: 2000 sccm</td>
<td>1150-1300</td>
<td>1.8 × 50 cm</td>
<td>Random</td>
<td>[35]</td>
</tr>
<tr>
<td>6</td>
<td>40 × 1200 mm</td>
<td>Ethanol, ferrocene, thiophene</td>
<td>120-600 ml/hr</td>
<td>Nitrogen: 32 LPH</td>
<td>1420</td>
<td>—</td>
<td>Random</td>
<td>[37]</td>
</tr>
<tr>
<td>7</td>
<td>50 mm</td>
<td>Methane (30 sccm), ferrocene, sulfur (1 wt%)</td>
<td>—</td>
<td>H₂: 4000 sccm</td>
<td>1100</td>
<td>Transparent film</td>
<td>Random</td>
<td>[41]</td>
</tr>
<tr>
<td>8</td>
<td>—</td>
<td>Methane, ferrocene, thiophene</td>
<td>—</td>
<td>H₂: 1500 sccm</td>
<td>1200</td>
<td>2 × 20 cm</td>
<td>Partially aligned</td>
<td>[42]</td>
</tr>
<tr>
<td>9</td>
<td>50 × 600 mm</td>
<td>Ethanol, ferrocene, thiophene</td>
<td>30 ml/hr and 60 ml/hr</td>
<td>Ar: 100 sccm H₂: 100-2400 sccm</td>
<td>1420</td>
<td>—</td>
<td>Random</td>
<td>[38]</td>
</tr>
<tr>
<td>10</td>
<td>60 mm</td>
<td>n-Hexane, ethanol, ferrocene, thiophene</td>
<td>60 ml/hr and 120 ml/hr</td>
<td>Nitrogen: 0.5–1 LPM</td>
<td>1300-1500</td>
<td>10 × 62 cm</td>
<td>Partially aligned</td>
<td>[43]</td>
</tr>
</tbody>
</table>
recorded using Mettler Toledo TGA instrument. The samples were heated up to 800°C in air with a heat ramp rate of 10°C/minute. The thickness of the sample was calculated manually using a calibrated screw gauge with least count of 0.001 mm. The electrical conductivity was calculated along both parallel and perpendicular using four probe method where the contacts were directly integrated into sample using silver paste and the measurements were performed at room temperature.

3. Results and Discussion

The synthesis process of CNTs has been explained mechanistically in three steps as shown in cartoon (Figure 2). The process initiates with the decomposition of ferrocene to give iron atoms which collide with other homo atoms to form iron cluster in nanodimensions [18, 44]. Thiophene further decompose in range of 600-800°C to release sulfur atoms which are reported to cover iron nanoparticles forming a Fe-S eutectic phase. These sulfur-coated nanoparticles arrest the size of catalyst and also enhance the solubility of hydrocarbon in iron thereby encouraging thermal pyrolysis [45]. The final step involves the thermal disintegration of hydrocarbon source for release of carbon atoms which forms a supersaturated solution in iron atom ultimately precipitating out as nanotubes on its surface.

Hydrogen gas has been a common byproduct in thermal decomposition reaction of ferrocene and ethanol; therefore, presence of external hydrogen environment suppresses their excessive decomposition by shifting the equilibrium towards reactant side [46, 47]. Reduced decomposition rates decelerate the formation of large size catalyst particles and amorphous carbon thereby improving the homogeneity and purity of synthesized nanotubes and encourage the formation of continuous aerogel as in our case.

Raman spectroscopy has been an important tool for evaluating the quality of CNT by estimating the ratio of intensity of graphitic peak (G-band) to that of defect peak (D band). An intense sharp G-band centered approximately at 1580 cm⁻¹ signifies the presence of highly ordered graphite structure [48]. The D band lying around 1303 cm⁻¹ reveals the presence of symmetry breaking defects as induced by sp³ carbon and amorphous state [49]. It is generally believed that the intensity ratio of G to D band can be used as a direct measure to quantify the purity of CNT. As can be seen from Figure 3(a), I_G/I_D value has been found to be 10.03 which express good quality with very low amorphous carbon and defects and can be attributed to cleansing rate of hydrogen gas which convert unwanted carbonaceous material to hydrocarbon gases.

Thermal oxidation temperature and bulk composition information is derived using TGA analysis. It can be seen in Figure 3(b) that considerable weight loss can be seen in
the TGA curve in the temperature range of 450-620°C, which depicts the oxidation of CNTs. A more clear indication of thermal stability is evidenced by the differential thermogravimetry curve where the peak minimum is found at 572°C. The residue which amounts for 12.1% left at higher temperature quantifies the iron oxide content in sample.

Figure 3: Raman spectroscopy analysis at 785 laser wavelength (a) and thermogravimetric analysis result (b) of as-produced CNT sheet sample.

Figure 4: As-prepared CNT sheet wound on aluminium foil (a). FE-SEM images of the sample demonstrating morphology and degree of alignment of nanotubes (b and c).
The corresponding iron content can be estimated using the stoichiometric relation in the given reaction [50].

\[ 4Fe + 3O_2 \rightarrow 2Fe_2O_3, \]  

which was found to be 8.47 wt%.

Further evidence of CNT purity comes from the overview of surface morphology of the sample seen in FE-SEM images as shown in Figure 4. Entangled bundled network of nanotubes having very large aspect ratio can be clearly seen under the microscope with presence of very few heteroimpurities. Further, the tubes can be seen running parallel with each other demonstrating considerable degree of alignment in the sample. Continuous deposition, facilitated by the hydrogen flow rate, ensures a regular stretching force onto the sample due to winding at larger rates which forcefully aligned the network accompanied by improved packing of bundles.

The quality of alignment of nanotubes has been further assessed through polarized Raman spectroscopy technique. Enhanced Raman signals are obtained when the incident laser beam is parallel polarized with the long axis of nanotube, while the signal intensity depletes as angle of rotation increases until perpendicular orientation. Ratio of G-peak intensities in both extreme orientation is referred as optical anisotropy, which is used to characterize the degree of alignment in the sample. Continuous deposition, facilitated by the hydrogen flow rate, ensures a regular stretching force onto the sample due to winding at larger rates which forcefully aligned the network accompanied by improved packing of bundles.

Figure 5: Anisotropic ratio as calculated by ratio of (a) G-peak intensity in polarized Raman spectra and (b) electrical conductivity values in parallel and perpendicular direction.
Figure 6: Continued.

Electron conduction
Along the tube
Inter tube (Via tunneling)
alignment of nanotubes [51]. Figure 5(a) reveals the polarized Raman spectra of the fabricated CNT sheet, and the ratio $I_{G}/I_{D}$ has been calculated to be 4.62 which indicates high degree of alignment in the structure.

The electrical conductivity of this sample was also calculated in different directions employing four probe conductivity measurement techniques to eliminate the role of contact resistance. Connections were prepared on the sample for attachment of probe using silver paste. The electrical conductivity was calculated using formula

$$\sigma = \frac{l}{Rtw}, \quad (2)$$

where $l$ is the distance between the probe, $R$ is the resistance, $t$ is the thickness, and $w$ is the width of sample.

Figure 5(b) gives the conductivity values of sheet along different orientation. The CNT sheet showed expected anisotropy in values when measured along different axis. The numerical value of conductivity was found to be $2.14 \times 10^4$ S/m along the direction of tube axis and $0.63 \times 10^4$ S/m in perpendicular direction. The ratio of conductivities in different orientation was calculated to be 3.39 which also indicates ease of flow of conducting carriers along the axis of nanotubes.

The general conduction mechanism of charge carriers through the CNT sheet has been explained in Figure 6. Fundamentally, the resistance inside the CNT network has been contributed by two factors: intratube resistance, i.e., intrinsic resistance of an individual nanotube, and intertube resistance, i.e., resistance at contact barriers. The former factor is governed by their respective helicities and the latter contribution occurs due to contact barriers induced by the misalignments, contacts, and defects along the nanotube where the conducting particle has to tunnel through the gap. During the charge transport, majority of carriers undergo the shortest conducting pathway having small junction length and minimal contact resistance between the CNTs [22, 52]. Alignment of nanotubes in a particular direction allows conductive transport of carriers when compared to random orientation in terms of decreased number and length of junction barrier as can be seen in Figures 6(a) and 6(b). Moreover, the aligned CNTs show decreased conductivity values when measured normal to running axis of nanotubes due to increased number of gaps from where the electron has to tunnel through. Figures 6(b) and 6(c) show the difference in the conductive pathway along the parallel and perpendicular direction in aligned CNT sheets.

In this study, we have fabricated a highly aligned macroscopic CNT sheet which can be explored in wide range of applications. The high magnitude conductivity as obtained in this study has been credited to compact and aligned bundling of CNTs along the parallel direction with reduced interfaces among CNT bundles, thus enhancing the ballistic conduction of charge carriers.

4. Conclusion

In summary, we have demonstrated the one step fabrication of high-quality CNT sheet having significant alignment of nanotubes at a fixed set of parameters. The high purity, crystallinity, and alignment have been the combined result of efficient selection of parameters and stretching force induced during the continuous winding of CNT aerogel. SEM images confirm the alignment, while the $I_{G}/I_{D}$ value of 10.03 indicated by Raman spectroscopy signifies high graphitization in the sample. Electrical conductivity values also show a large magnitude conferring to the longer tube length with decreased number of intercontact points of nanotubes, thus enhancing the transport of electrons. Alignment ratio $I_{G}/I_{D}$/
Data Availability

Data can be provided on request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

Acknowledgments

Manoj Sehrawat and Mamta Rani gratefully acknowledge their research fellowships received from the CSIR and UGC India, respectively. Authors are thankful to Dr. Nita Dilawar and Mr. Jasjeer Singh for polarized Raman studies, Dr. H.K. Singh for four probe conductivity measurements, Mr. R.K. Seth for TGA analysis, Mrs. Shaveta Sharma for Raman spectroscopy, and Mr. Naveal Kishore for electron microscopy studies. This study is self-funded.

References


