Plasma-electric field controlled growth of oriented graphene for energy storage applications

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Abstract

It is well known that graphene grows as flat sheets aligned with the growth substrate. Oriented graphene structures typically normal to the substrate have recently attracted major attention. Most often, the normal orientation is achieved in a plasma-assisted growth and is believed to be due to the plasma-induced \textit{in-built} electric field, which is usually oriented normal to the substrate. This work focuses on the effect of an \textit{in-built} electric field on the growth direction, morphology, interconnectedness, structural properties and also the supercapacitor performance of various configurations of graphene structures and reveals the unique dependence of these features on the electric field orientation. It is shown that tilting of growth substrates from parallel to the normal direction with respect to the direction of \textit{in-built} plasma electric field leads to the morphological transitions from horizontal graphene layers, to oriented individual graphene sheets and then interconnected 3D networks of oriented graphene sheets. The revealed transition of the growth orientation leads to a change in structural properties, wetting nature, types of defect in graphitic structures and also affects their charge storage capacity when used as supercapacitor electrodes. This simple and versatile approach opens new opportunities for the production of potentially large batches of differently oriented and structured graphene sheets in one production run.

Keywords: graphene, PECVD, growth, energy storage

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene and its derivatives open new avenues for academic as well as industrial research, due to their remarkable physical and chemical properties [1–5]. The recent trend is to transform graphene structures from 2D to 3D, often referred to in the literature as carbon nanowalls, few-layered graphene nanoflakes, graphitic petals and vertical graphene nanosheets (VGN) [6–9]. It is a 3D interconnected network of few-layer graphene sheets standing normal to the substrate. These 3D structures open up new ways to explore the effects of the surfaces, reactive edges, substantially increased
surface-to-volume ratio and reactivity compared to substrate-supported planar graphenes [5, 6]. Along with the intriguing properties of graphene, the most interesting characteristics of this structure include excellent mechanical [10], optical [11, 12], thermal [13], electrical [14, 15] and magnetic properties [8], long-term stability [16], bio-compatibility [17], capability of easy functionalization [18] and several others. The self-organized VGN with the aforementioned properties emerged as an attractive advanced functional material for electron field emission, energy storage and other applications [18–27]. To realize their potential in nanoscale devices, substantial effort has been made and continues to be made to design the VGN structures with high yield, optimized inter-sheet spacing and desired properties.

As a result of the emerging demand for graphene synthesis, the plasma-enhanced chemical vapor deposition (PECVD) technique has been regarded as an effective and widely used method [15, 28, 29]. However, understanding the science behind the plasma-assisted growth with deterministic morphology and property is essential according to the technological and scientific viewpoint. The in-built electric field is believed to be the key factor for the growth of carbon nanostructures in a vertical orientation [9, 30–33]. Despite the immense advances in the field, much less attention has been paid to the investigation of the dependency of growth on plasma-induced in-built electric field [34–36]. The straight and aligned VGN with regular inter-sheet spacing was obtained on the substrate perpendicular to the electrode [34], while similar morphological vertical graphene on Au/AIO/Si, but not on bare Si and Cu substrate, are observed in [35]. The alignment mechanism was attributed to the surface-plasmon effects [35]. A recent study demonstrated the switching of graphene growth direction from vertical to horizontal by using a custom-designed copper-foam-based Faraday cage [37]. The purpose of designing the Faraday cage was to reduce the plasma-induced ion bombardment, eliminate the electric field effect and achieve a uniform electric field distribution.

On the other hand, the growth direction of graphene was found to be strongly polarized by the electric field direction and hence random distribution in the vertical sheets is observed, while the substrate is placed horizontally [38]. A similar result was also reported in the case of carbon nanotubes (CNTs) and explained by the torque experienced along the tube axis upon changing the substrate orientation [39]. Interestingly, Bower et al [40] demonstrated the growth of CNTs parallel to the surface normal of the substrate irrespective of substrate orientation and shape (flat or concave). Apart from graphene and CNT, Lin et al [41] demonstrated the change in orientation of carbon nanofiber with respect to the angle between the substrate surface and in-built electric field. The concluding remarks from these reports cover the direction of electric field influence on the growth orientation. Therefore, control over the electric field direction is essential to grow VGN structures with a desired orientation.

In general, during the VGN growth in PECVD, the directions of both the plasma and in-built electric fields are parallel to the surface normal of the substrate, as shown in scheme 1(a). Importantly, because of the relatively high rates of production and delivery of diverse building units in a plasma, it is quite challenging to achieve thin planar graphene layers using the PECVD technique [42–44]. However, recent reports on planar graphene growth in PECVD, where the substrate was kept such that the plasma direction/electric field direction was perpendicular to the substrate surface normal, is depicted in scheme 1(b) [42–44]. It is also possible to grow planar graphene structure in a former arrangement by choosing the appropriate gas composition, substrate temperature, plasma power and deposition time [7, 45, 46]. However, both the vertical and planar graphene structures have profound aspects depending upon the kind of application. For example, VGN is envisioned material for energy storage and field emission applications [6] whereas, planar nanographitic (PNG) films are suited to charge trapping memory and transparent heating devices [37, 47].

The existing background art and the many unanswered questions related to the growth process of VGN, make us pose the following questions and attempt to clarify them in this dedicated study.

(i) What is the role of an in-built electric field in controlling the growth orientation and is the normal graphene sheet orientation to the growth substrate primarily due to in-built electric field?

(ii) How does the direction of electric field affect the orientation, morphology, and structure of graphenes grown under the same other process conditions?

(iii) How does the arising variation in the structural, morphological and wetting properties, and the defect presence affect the performance of such graphene materials as electrodes for advanced energy storage devices?

Focusing on addressing these critical questions, we endeavor to grow graphene on SiO2/Si substrate placed at different inclinations, simultaneously, in the PECVD system. The morphology and structural investigations were carried out. This study evidenced the significant role of plasma-induced in-built electric field by flipping the growth from vertical to planar graphene by just inclining the surface normal of the substrate from 0° to 90°. The influence of growth orientation on their performance as supercapacitor electrodes is demonstrated. Herein, we envisaged the possibility of tuning the growth orientation of graphene structures towards extending its potential utilization over a wide range of applications.

2. Experimental methodology

2.1. Growth of graphene

Towards addressing the issue of in-built electric field orientation growth in plasma, we carried out growth of graphene on substrates with different inclinations, simultaneously. To achieve this, we designed a multi-angled faceted Cu block with surfaces at different angles of inclination (θ) namely 0°, 30°, 45°, 60° and 90°, as depicted in figure 1(a). The angle of inclination (θ) is defined as an angle between the surface normal of the substrate and plasma-induced inherent electric field (figure 1(a)). Thermally oxidized Si is used as the
substrate and is placed on the Cu block on each edge. The block is placed on the heater stage and the substrates are tightened by screws. We grow graphene structures on SiO2/Si substrate using an electron-cyclotron resonance (ECR)-PECVD technique and the details of the growth parameters were described in our previous report [7]. In brief, the deposition chamber was evacuated to $10^{-6}$ mbar, using a turbo molecular pump backed by a rotary pump. Thereafter, the substrate was heated for 4 h before starting the growth at 800 °C. It is anticipated that all surfaces of the Cu block experience uniform temperature because of its high thermal conductivity. The distance of the heater and plasma ignition point was 30 cm and this was maintained during the process. Pre-cleaning of the substrate was carried out by purging Ar gas with a 20 sccm flow rate at microwave plasma of 375 W. The deposition of carbon species was performed by feeding CH4 of 5 sccm for 30 min along with Ar carrier gas at the same temperature and microwave power. The observed operating pressure was $10^{-3}$ mbar during the growth. The plasma and gas flow were turned off and the substrates were allowed to anneal for 30 min at the same temperature and base pressure to achieve a better quality film [48]. Thereafter, the substrates were allowed to cool down to room temperature naturally and were taken out of the chamber for further characterization.

2.2. Characterization

The surface morphology of the as-grown graphene structures was inspected by field-emission scanning electron microscopy (FESEM, Supra 55, Zeiss, Germany). High-resolution transmission electron microscopy (HRTEM, LIBRA 200 FE, Zeiss, Germany) was adopted in order to investigate the microstructure and number of graphene layers in each sheet. Wetting properties of the as-grown film were studied by releasing a water drop with volume 1 µl and the corresponding contact angle was measured (Apex Instrument Co. Pvt. Ltd., India). The morphological analysis in terms of density, height and length of vertically oriented graphene sheets, as well as water contact angle for the film grown at a different angle of inclination.

Figure 1. (a) Photographic image of the designed Cu block with a different angle of inclination from 0° to 90°. Angle is defined between in-built electric field or plasma direction and normal of the substrate surface. (b)–(f) Scanning electron micrograph of graphene structure grown at a different angle with respect to the plasma direction. (g) Micrograph of vertical graphene grown directly on the heater surface and inset represents its cross-sectional view. (h) Average vertical sheet density, average length and average height of vertical sheets and (i) water contact angle for the film grown at a different angle of inclination.

Scheme 1. Schematic of PECVD for the growth of (a) vertical graphene and (b) planar graphene.
The degree of graphitization of the film was investigated by Raman spectroscopy (inVia Renishaw, UK). Raman spectra of the films were collected using 532 nm excitation, a 50× objective lens and monochromator with a grating of 1800 grooves mm⁻¹. The areal capacitance of the graphene structures grown at different angles of inclination was estimated by cyclic voltammetry. The cyclic voltammogram was carried out in a three-electrode configuration using a Metrohm Autolab workstation (model PGSTAT302N, Netherlands). A 1 × 1 cm² area of film was used as the working electrodes, whereas platinum foil and Ag/AgCl (KCI saturated) were used as the counter and reference electrodes, respectively. The aqueous H₂SO₄ solution was used as an electrolyte. The areal capacitance (C in F cm⁻²) was estimated from a cyclic voltammogram using

\[ C = \left( \int I dV \right) / 2V \cdot v \cdot s, \quad (1) \]

where I, V, v and s are current density, potential window, scan rate and exposed area of an electrode, respectively.

3. Results

3.1. Morphological analysis

The FESEM micrographs of the graphitic structures are presented in figures 1(b)–(f). A flipping in morphology from 3D vertical graphene to the planar structure with increased angle of inclination (0° to 90°) is evidenced. With the same motivation, tuning the morphology from vertical to horizontal was obtained by using a custom-designed copper-foam-based Faraday cage [37]. However, designing of a Cu block with a different angle is very simple and cost-effective. In addition, our method produces both kinds of graphene structures in a single growth run, which we believe is of technological interest. The growth of an interconnected and vertically aligned 3D graphene sheet network is found, while the surface normal of the substrate and electric field are parallel, as shown in figure 1(b). In contrast, the PNG film with a very small number of vertically oriented flakes is obtained in the perpendicular configuration, as shown in figure 1(f). The observed results clearly indicate the significant influence of the angle of inclination on the growth orientation. This result is in good agreement with the observation of the existing literature on plasma-induced tuning of the growth orientation in the case of carbon fiber and carbon tubes [40, 41]. Here, we assumed that the top surface of the Cu block experienced the same temperature irrespective of the angle of inclination, since the block is only 1 cm thick and kept at 800 °C for 4 h before starting the growth to achieve a uniform temperature. We also excluded the effect of the height difference. However, to avoid ambiguity, we reconfirmed our findings by growing the film on the Cu block (0°) and on the heater surface, simultaneously. For comparison sake, we have shown the morphology of VGN grown on the top (0°) of the Cu block and VGN grown directly on the heater surface (0°) in figures 1(b) and (g), respectively. There is no significant change in the morphology observed, except for a slight variation in areal density. We also investigated the growth of VGN with respect to the distance between the plasma source and substrate surface in our previous report [7]. To ensure reproducibility and repeatability, the synthesis of graphene under the same conditions, except the deposition time, is carried out. The detail of the experimental result is provided in figure S1 of the supplementary material (stacks.iop.org/JPhysD/51/145303/mmedia). Hence, the statistics of the experimental results justified the influence of in-built plasma-induced electric field orientation on VGN growth and the possible explanation is discussed in the subsequent paragraphs.

The FESEM micrographs (figure 1(b)–(f)) demonstrated the possibility of growing interconnected VGN, free-standing VGN and PNG in a single growth process. As the angle of inclination reduces from 90° to 0°, the observed variations in morphology are: (i) flipping the growth from PNG to VGN, (ii) more nucleation of vertical sheets, (iii) increase in height of the sheets and (iv) merging of vertical sheets resulted in longer vertical sheets. The vertical height of the VGN is examined by cross-sectional micrograph, as shown in the inset of figure 1(g). Average sheet density, average length and height of the vertical sheets for the film grown at different inclinations are plotted in figure 1(h). The morphological inspection of the as-grown films is also carried out via water contact angle measurement. It can be seen that the contact angle of the film drops down from 129° to 81° as the film changed its orientation from vertical to planar. Hence, the change in wettability of the films is attributed to the variation in surface morphology (figure 1(i)).

Figures 2(a)–(d) depict the HRTEM micrographs of both PNG and VGN samples, respectively. It is clearly observable that the NG layer in PNG consists of around 40 graphene layers with interlayer spacing of 0.367 nm. Whereas, it is 3–10 graphene layers with interlayer spacing of 0.343 nm in the case of VGN structures. In both cases, the interlayer spacing is higher than that of graphite (0.334 nm) and confirms its turbostratic graphitic structure.

3.2. Raman spectra analysis

In order to study the crystallinity and chemical structure, Raman spectra are recorded in the frequency range of 1000–3500 cm⁻¹ for all the samples. All the Raman spectra are normalized with respect to the G-peak intensity and plotted in figure 3(a). The typical Raman spectra of PECVD-grown graphene consists of a D-peak at 1350 cm⁻¹, G peak at 1580 cm⁻¹ and G' peak around 2700 cm⁻¹ [49, 50]. The presence of the G-peak is attributed to the in-plane stretching vibration (E₂g symmetry) in sp² bonded carbon. The double and triple resonances are responsible for the G'-peak. The presence of the G- and G'-peak affirms the graphitic nature of the grown samples [51]. On the other hand, the D-band is associated with the out-of-plane breathing mode (A₁g) of the sp³ bonded carbon. The D-band along with its overtones D' (ca. 1620 cm⁻¹) and D + D' (ca. 2950 cm⁻¹) are attributed to the edges, point defects such as vacancies, impurities, C–H sp³ bonded defects, grain boundaries, atmosphere-adsorbed molecular doping and folding/bending in the structure [50].
The striking observation from the Raman spectra is the reduction in intensity of the D-peak, merging the shoulder of the D′ peak with the G-peak and red-shift of the G-peak position around 8 cm$^{-1}$, as the structure transformed from vertical to planar. In addition, the G′ peak of all the structures fitted with a single Lorentzian line shape, which indicates the presence of stacking faults or turbostratic structure. This is consistent with the information obtained from the HRTEM analysis. The peak position and full width at half maximum (FWHM) of the D-, G- and G′ peaks that are extracted from the Raman spectra are plotted in figure 3(b). A change in the FWHM of the D-, G- and G′ as well as the peak position of the G-peak can be used to test the quality of graphene, in particular, the number of graphene layers, nature and number of defects, stress present in the film, and so forth [49–52]. The variations in the above parameters of the studied graphene samples can be correlated with graphitic quality, edge density and point defects. A high-intensity D-peak of VGN compared to PNG is attributed to the large density of edges. Whereas, broadened FWHM of the D-, G- and G′ in PNG can be attributed to the existence of larger numbers of grains and graphene layers as well as the higher amount of sp$^3$ content. These features are clearly evident from the morphological analysis (figures 1(f), 2(a) and (b)) [51]. To validate these conclusions, the sp$^3$ content is estimated from the following equation [7, 53]:

$$sp^3 \text{ content(\%)} = \left[0.24 - 48.9(\omega_G - 1580) \times 10^{-4}\right] \times 100$$

(2)

where $\omega_G$ is the FWHM of the graphene sample and the peak position of the G peak of graphene (1580 cm$^{-1}$) is taken as the reference. The obtained sp$^3$ content for the well-controlled VGN and PNG are 17% and 21%, respectively (table S1 in supplementary material). It can be seen that the change in geometry from VGN to PNG resulted in broadening in the FWHM of the D-, G- and G′ peaks. The broadening in the FWHM and red-shift of the G-peak position are attributed to the defects. In particular, the PNG structure is subjected to more strain due to the stress relaxation through the grain boundary as well...
Moreover, the intensity ratio of the D-to-G peaks \( (I_D/I_G) \) is estimated and plotted in figure 3(b). The obtained \( I_D/I_G \) ratios for VGN and PNG are 2.8 and 1.9, respectively. Based on the existing literature, this measured value implies that VGN contains vacancy-like defects whereas boundary-like defects dominated in PNG [56]. This result correlates well with the PNG morphology that contains a large number of grain boundaries (figure 1(f)).

3.3. Performance as supercapacitor electrodes

In order to find out the correlation between geometry and energy storage capacity, cyclic voltammetry studies were carried out on all the samples. The measured cyclic voltammograms are depicted in figure 4(a). It has been clearly seen that as the graphene structure transformed orthogonally to the substrate with perfect alignment, the current response under cyclic voltammetry substantially increased. The areal capacitance of the graphene films is estimated using equation (1) and plotted in figure 4(b). The areal capacitance of VGN is found to be 95.4 \( \mu \text{F cm}^{-2} \); it is roughly eight times higher compared to the PNG structure (13.1 \( \mu \text{F cm}^{-2} \)). The charge storage capacitance can further be improved by controlling the inter-sheet spacing and choosing a proper electrolyte [21, 57–59]. However, the well-controlled VGN demonstrated higher capacitance than the pristine defected graphene (7.5 \( \mu \text{F cm}^{-2} \)) as well as N-doped defected graphene (20.5–56.6 \( \mu \text{F cm}^{-2} \)) [55]. To emphasize the importance of the vertical structure, the volumetric capacitance is estimated by dividing the height of the vertical graphene structure by the areal capacitance and is expressed in terms of F cm\(^{-3} \) (figure 4(b)). A similar trend is observed for the volumetric capacitance of graphene-related structures. The obtained volumetric capacitance of VGN structures, grown with an inclination angle of 0°, is 6.4 F cm\(^{-3} \). On the other hand, the PNG shows a volumetric capacitance of 0.9 F cm\(^{-3} \). In general, hydrophilic graphene structures possess a higher capacitance. However, the hydrophilic PNG graphene exhibited lower capacitance compared to the vertical graphene. In addition, it was shown that the presence of multiple vacancies can enhance the density of states and lead to improved capacitance [55]. Noteworthy, is that VGN structures contain vacancy-like defects, as evidenced by the Raman spectroscopic analysis. Therefore, the higher charge storage capacity of VGN is attributed to the high surface-to-volume ratio, plenty of edges, better crystallinity and existence of vacancy-like defects. The observed results emphasize that the vertical orientation of graphene structures is preferred over horizontal when it comes to charge storage applications.

4. Discussion

The mechanism behind flipping in the growth orientation of graphene structure under the influence of in-built electric field is as follows. It is well known that plasma, the fourth state of matter, consists of ions, radicals, electrons and neutrals, etc. Due to their lighter mass, electrons are more mobile and hence the surface of all the floating materials including deposition substrates acquire a negative electric charge. Therefore, an in-built electric field is induced by the plasma onto the substrate surface [60]. Furthermore, this electric field acts as the driving force to attract the positive ions towards the substrate surface, in this case carbon ions/radicals are deposited onto the substrate. As the growth proceeds, a thin PNG layer forms on the substrate in the first stage. Formation of an electrically continuous PNG within a fraction of second growth is observed in our previous report [45].

It is also worth emphasizing that the growth of graphene-related structures using PECVD is the balance between the deposition of carbon species and etching process by atomic hydrogen. Hence, the thickness of the PNG layer is limited.
Herein, we have also observed a growth of PNG layer with a few randomly nucleated vertical sheets, while the surface normal of the substrate is kept perpendicular to the in-built electric field direction (inclination angle is 90°). Nucleation of vertical sheets is attributed to the stress released through the grain boundary of the NG islands as well as lattice mismatch between the substrate and NG layer.

On the other hand, when the substrate surface normal is parallel to the in-built electric field direction (inclination angle is 0°), an upward pull by the electric field along with the stress, preferential radical diffusion, crowding effect and lattice mismatch lead to faster growth of the vertical graphene sheets [9, 29, 61]. The strength of this upward force determines the alignment, ordering and growth rate of vertically oriented carbon nanostructures in the PECVD [36]. The upward pull \( F \) is directly proportional to the cosine of the inclination angle \( \cos \theta \) via the relation: \( F \propto E \cos \theta \), \( E \) is the in-built electric field due to plasma. Therefore, the maximum upward pull is experienced by the horizontally placed substrate, which leads to an interconnected network of VGN. The strength of the plasma-assisted upward pulling force is reduced upon increasing the inclination angle. In the case of the vertically placed substrate, the upward pull is zero, hence the growth is stopped after the initial nucleation of continuous PNG films. The quantification of the electric field strength with respect to the substrate surface orientation has yet to be investigated. Since, in our previous report, we demonstrated that the type of substrate only has influence on the growth rate [62], we anticipated the validity of the obtained results irrespective of the substrate material. Hence, this fact clearly evidenced that the angle of inclination of electric field has a predominant role in tuning the morphology from planar to vertical graphene and hence its graphic quality, wettability and energy storage capacity, which is of particular importance for the development of plasma-assisted nanofabrication processes and associated equipment and instrumentation [63].

5. Conclusion

In summary, we have demonstrated that the flipping in growth orientation of graphene structures by simultaneous growth on SiO₂/Si substrates with different inclinations is achieved by a multi-angle faceted Cu substrate holder in the ECR-PECVD technique. The vertically aligned graphene is realized, while placing the surface normal of the substrate parallel to the in-built electric field. In contrast, the PNG structure is grown, while the surface normal of the substrate is perpendicular to the in-built electric field. The growth rate and dimension of the sheets of VGN showed a strong dependency on the inclination angle of the electric field. The dramatic change in growth orientation of graphene structures is corroborated with the strength of the in-built electric field. A significant influence of growth orientation on the structural and wetting properties is evidenced. These features in turn affect the performance of graphene sheets with different orientation and structures as electrodes in supercapacitor energy storage devices. Interestingly, the capacitance of VGN is measured to be 95 µF cm⁻², which is approximately eight times higher than that of the PNG structure (13 µF cm⁻²). This study offers a simple, versatile and easily scalable process for the effective control of the morphological and structural properties of graphene sheets and layers and can be used for the customized production of batches of graphenes of very diverse types and properties in the same process run.

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Author contributions

SG and SRP conceived the idea and performed the experiments. SG, SRP and KO contributed to the data analysis, interpretation and manuscript preparation. All authors discussed the results, commented on the manuscript and gave approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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References

[1] Mitra S, Banerjee S, Datta A and Chakravorty D 2016 A brief review on graphene/inorganic nanostructure composites: materials for the future Indian J. Phys. 90 1019–32
[2] Ferrari A C, Bonaccorso F, Fal’ko V, Novoselov K S, Roche S, Beggild P, Borini S, Koppens F H, Palermo V and Pugno N 2015 Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems Nanoscale 7 4598–810
[3] Kataria S, Wagner S, Ruhkopf J, Gahoi A, Pandey H, Bornemann R, Vaziri S, Smith A D, Ostling M and Lemme M C 2014 Chemical vapor deposited graphene: from synthesis to applications Phys. Status Solidi A 211 2439–49
[4] Singh V, Joung D, Zhai L, Das S, Khondaker S I and Seal S 2011 Graphene based materials: past, present and future Prog. Mater. Sci. 56 1178–271
[5] Bo Z, Mao S, Jun Han Z, Cen K, Chen J and Ostrivok K 2015 Emerging energy and environmental applications of vertically-oriented graphenes Chem. Soc. Rev. 44 2108–21
[6] Srivastava S K, Kumar V and Vankar V 2018 Carbon nanowalls: a potential 2-dimensional material for field emission and energy-related applications Nanomaterials and Their Applications (Berlin: Springer) pp 27–71
[7] Ghosh S, Polaki S R, Kumar N, Amirthapandian S, Kamruddin M and Ostrivok K 2017 Process-specific mechanisms of vertically oriented graphene growth in plasmas Beilstein J. Nanotechnol. 8 1658–70
[8] Soin N, Ray S C, Sarma S, Mazunder D, Sharma S, Wang Y F, Pong W F, Roy S S and Strydom A M 2017 Tuning the electronic and magnetic properties of nitrogen-functionalized few-layered graphene nanoflakes J. Phys. Chem. C 121 14073–82
[9] Zhu M, Wang J, Holloway B C, Outlaw R, Zhao X, Hou K, Shuthananandan V and Manos D M 2007 A mechanism for carbon nanosheet formation Carbon 45 2229–34
[10] Davami K, Jiang Y, Cortes J, Lin C, Shaygan M, Turner K T and Bargatin I 2016 Tuning the mechanical properties of vertical graphene sheets through atomic layer deposition Nanotechnology 27 155701
[11] Evlashin S, Syvakhovskiy S, Suetin N, Pilevsky A, Murzina T, Novikova N, Stepanov A, Egorov A and Rakhimov A 2014 Optical and IR absorption of multilayer carbon nanowalls Carbon 70 111–8
[12] Sivadasan A K, Santanu P, Subrata G, Ramanathaswamy P and Sandip D 2017 Spectroscopically forbidden infra-red emission in Au-vertical graphene hybrid nanostructures Nanotechnology 28 465703
[13] Mishra K K, Ghosh S, Thogulvuta R A, Amirthapandian S and Kamruddin M 2016 Thermal conductivity and pressure-dependent Raman studies of vertical graphene nanosheets J. Phys. Chem. C 120 25092–100
[14] Pawan K 2017 Temperature-dependent conduction mechanism of vertically aligned graphene nanoflakes incorporated with nitrogen in situ Mater. Res. Express 4 075011
[15] Ghosh S, Polaki S R, Krishna N G and Kamruddin M 2018 Influence of nitrogen on the growth of vertical graphene nanosheets under plasma J. Mater. Sci. 53 7316–25
[16] Ghosh S, Polaki S R, Ajikumar P, Krishna N G and Kamruddin M 2017 Aging effects on vertical graphene nanosheets and their thermal stability Indian J. Phys. 92 437–42
[17] Raluca I, Sorin V, Catalin L, Anisoara C and Gheorghe D 2016 Vertically, interconnected carbon nanowalls as biocompatible scaffolds for osteoblast cells J. Phys. D: Appl. Phys. 49 274004
[18] Ghosh S, Gupta B, Ganesan K, Das A, Kamruddin M, Dash S and Tyagi A K 2016 MnO2-vertical graphene nanosheets composite electrodes for energy storage devices Mater. Today Proc. 3 1686–92
[19] Prasad K, Bandara C, Kumar S, Singh G, Brockhoff B, Bazaka K and Ostrivok K 2017 Effect of precursor on antifouling efficacy of vertically-oriented graphene nanosheets Nanomaterials 7 170
[20] Soin N, Sinha Roy S, Roy S, Hazra K S, Misra D S, Lim T H, Hetherington C J and McLaughlin J A 2011 Enhanced and stable field emission from in situ nitrogen-doped few-layered graphene nanoflakes J. Phys. Chem. C 115 5366–72
[21] Ghosh S, Mathews T, Gupta B, Das A, Krishna N G and Kamruddin M 2017 Supercapacitive vertical graphene nanosheets in aqueous electrolytes Nano-Struct. Nano-Objects 10 42–50
[22] Ray S C, Soin N, Makgato T, Chuang C, Pong W, Roy S S, Ghosh S K, Strydom A M and McLaughlin J 2014 Graphene supported graphene/graphane bilayer nanostructure material for spintronics Sci. Rep. 4 3862
[23] Krivchenko V, Evlashin S, Mironovich K, Verbiskiy N, Nefedov A, Woll C, Kozenkova A Y, Suetin N, Syvakhovskiy S and Vyalikh D 2013 Carbon nanowalls: the next step for physical manifestation of the black body coating Sci. Rep. 3 3328
[24] Lee W J, Jeong S, Lee H, Kim B J, An K H, Park Y K and Jung S-C 2017 Facile synthesis of iron-ruthenium bimetallic oxide nanoparticles on carbon nanotube composites by liquid phase plasma method for supercapacitor Korean J. Chem. Eng. 34 2993–8
[25] Jin E M, Lee H J, Jun H B and Jeong S M 2017 Electrochemical properties of α-Co(OH)2/graphene nanoflake thin film for use as a hybrid supercapacitor Korean J. Chem. Eng. 34 885–91
[26] Simon P and Gogotsi Y 2008 Materials for electrochemical capacitors Nat. Mater. 7 845–54
[27] Ghosh S, Sahoo G, Polaki S R, Krishna N G, Kamruddin M and Mathews T 2017 Enhanced supercapacitance of activated vertical graphene nanosheets in hybrid electrolyte J. Appl. Phys. 122 214902
[28] Ostrivok K K, Cvelbar U and Murphy A B 2011 Plasma nanoscience: setting directions, tackling grand challenges J. Phys. D: Appl. Phys. 44 174001
[29] Bo Z, Yang Y, Chen J, Yu K, Yan J and Cen K 2013 Plasma-enhanced chemical vapor deposition synthesis of vertically oriented graphene nanosheets Nanoscale 5 5180–204
[30] Levchenko I, Ostrivok K, Rider A, Tam E, Vladimirov S and Xu S 2007 Growth kinetics of carbon nanowall-like structures in low-temperature plasmas Phys. Plasmas 14 063502
[31] Kar R, Patel N, Chand N, Shilpa R, Dusane R, Patil D and Sinha S 2016 Detailed investigation on the mechanism of co-deposition of different carbon nanostructures by microwave plasma CVD Carbon 106 233–42
[32] Levchenko I, Ostrivok K, Keidar M and Xu S 2005 Microscopic ion fluxes in plasma-aided nanofabrication of ordered carbon nanotip structures J. Appl. Phys. 98 064304
[33] Xu S, Levchenko I, Huang S Y and Ostrivok K 2009 Self-organized vertically aligned single-crystal silicon nanostructures with controlled shape and aspect ratio by reactive plasma etching Appl. Phys. Lett. 95 111505
[34] Hiramatsu M and Hori M 2006 Fabrication of carbon nanowalls using novel plasma processing Japan. J. Appl. Phys. 45 5522
[35] Wu Y and Yang B 2002 Effects of localized electric field on the growth of carbon nanowalls Nano Lett. 2 355–9
[36] Neyes E C, van Duin A C and Bogaerts A 2011 Insights in the plasma-assisted growth of carbon nanotubes through atomic scale simulations: effect of electric field J. Am. Chem. Soc. 134 1256–60
[37] Qi Y et al 2017 Switching vertical to horizontal graphene growth using Faraday cage-assisted PECVD approach for high-performance transparent heating device Adv. Mater. 30 1704839
[38] Zhang Y, Tang S, Deng D, Deng S, Chen J and Xu N 2013 Growth direction manipulation of few-layer graphene in the vertical plane with parallel arrangement Carbon 56 103–8
[39] Zhang Y, Chang A, Cao J, Wang Q, Kim W, Li Y, Morris N, Yeimle E, Kong J and Dai H 2001 Electric-field-directed growth of aligned single-walled carbon nanotubes Appl. Phys. Lett. 79 3155–7
[40] Bower C, Zhu W, Jin S and Zhou O 2000 Plasma-induced alignment of carbon nanotubes Appl. Phys. Lett. 77 830–2
[41] Lin C-C, Lee I-C, Yen J-H and Hon M-H 2004 Sheath-dependent orientation control of carbon nanofibres and
carbon nanotubes during plasma-enhanced chemical vapour deposition Nanotechnology 15 176

[42] Van Nang L and Kim E-T 2012 Controllable synthesis of high-quality graphene using inductively-coupled plasma chemical vapor deposition J. Electrochem. Soc. 159 K93–6

[43] Nandamuri G, Rouminov S and Solanki R 2010 Remote plasma assisted growth of graphene films Appl. Phys. Lett. 96 154101

[44] Ghosh S, Ganesan K, Polaki S R, Ravindran T, Krishna N G, Kamruddin M and Tyagi A 2014 Evolution and defect analysis of vertical graphene nanosheets J. Raman Spectrosc. 45 642–9

[45] Ghosh S, Ganesan K, Polaki S R, Ilango S, Amirthapandian S, Dhara S, Kamruddin M and Tyagi A K 2015 Flipping growth orientation of nanographitic structures by plasma enhanced chemical vapor deposition RSC Adv. 5 91922–31

[46] Meng J, Yang R, Zhao J, He C, Wang G, Shi D and Zhang G 2015 Nanographene charge trapping memory with a large memory window Nanotechnology 26 455704

[47] Casiraghi C 2011 Raman intensity of graphene Phys. Status Solidi b 248 2593–7

[48] Malard L, Pimenta M, Dresselhaus G and Dresselhaus M 2009 Raman spectroscopy in graphene Phys. Rep. 473 51–87

[49] Karuppiah G, Ghosh S, Krishna N G, Ilango S, Kamruddin M and Tyagi A K 2016 A comparative study on defect estimation using XPS and Raman spectroscopy in few layer nanographitic structures Phys. Chem. Chem. Phys. 18 22160–7

[50] Ostrikov K, Long J D, Rutkeyvych P P and Xu S 2006 Synthesis of functional nanoassemblies in reactive plasmas Vacuum 80 1126–31

[51] Nanotechnology 15 176