A novel approach towards selective bulk synthesis of few-layer graphenes in an electric arc

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Abstract
The paper demonstrates the selective bulk synthesis of few-layer graphenes by optimizing an external magnetic field assisted electric arc. An ultra-high purity glassy graphite anode was sublimated in an argon atmosphere, and carbon nanotubes (CNTs), along with graphene sheets, were found inside the deposit formed on the cathode. Both the high purity CNTs and the graphene sheets, with minimal structural defects, were synthesized separately by varying the strength and orientation of the external magnetic field. The as-synthesized carbonaceous samples were characterized with the help of transmission electron microscopy, selected area electron diffraction (SAED), Raman spectroscopy and thermogravimetry with the objective of optimizing the highest selective production of 2D graphene structures. The as-synthesized graphene sheets exhibited a relatively high degree of graphitization and low structural defect density as confirmed by Raman spectroscopy. They were found to exhibit higher oxidation temperature ($767 \degree C$) than that of the carbon nanocrystalline particles ($690 \degree C$), as inferred from the thermogravimatric analysis. Moreover, they were found to roll up at their edges on account of their surface energy minimization. This was confirmed by the SAED analysis. With this new technique, we could successfully synthesize 2D graphene structures at the rate of a few g h⁻¹.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The first historical isolation of single-layer graphene from the crystalline graphite was demonstrated by Novoselov et al in 2004 [1]. Since then, graphene has stimulated a deluge in carbon research because of its unusual physical and electronic properties [2]. It has been demonstrated that inside graphenes, the electrons behave as mass-less Dirac fermions [3] and a room temperature quantum Hall effect can be realized within graphenes [4]. Moreover, these studies [1–4] have indicated the novelty of graphene for their unusually high electron mobility. However, the production methods of graphenes suffer from the serious problem of lack of an eco-friendly way to produce the material at a large scale, commensurate with the application areas [5, 6]. There are currently three approaches to synthesize graphenes—mechanical or chemical exfoliation of pure graphite [1, 7], epitaxial growth by vapour phase deposition of hydrocarbons or CO on metal substrates [8–11] and thermal annealing of SiC substrates [12], each one
of which involves the top-down approach. In the current world scenario, chemical synthesis methods have an edge due to their large scale synthesis potentials. However, the chemical routes are riddled with the issues of bio-compatibility. This paper demonstrates the synthesis of high-quality graphenes directly from the gas phase condensation of carbon precursors, using a rotating electric-arc technique. The quality of the product is shown to contain low defects, wherein, the production rate is appreciably high (a few g h$^{-1}$). The process generates various carbon allotropes with no production of any toxic gas or hazardous chemical as by-products being liberated to the environment, and is thus very much eco-friendly.

Arc synthesis part of novel carbon nanostructures, such as fullerenes [13] and carbon nanotubes (CNTs) [14], has been known to yield the best quality products [15]. Among the various arc manipulation schemes available, magnetic field assisted electric arc is an interesting area of research for both plasma physicists and nanotechnologists [16–18]. Though, many reported works in the literature have addressed the effects of an external magnetic field on the formation of arc derived CNTs [19–21], none of them has addressed the following issues:

(i) growth of carbon nanostructures when a carbon arc is superimposed with a steady non-uniform magnetic field with variable radial and axial components;
(ii) feasibility of synthesizing a variety of carbon nanostructures (CNTs, graphene sheets etc) through a suitable combination of electric and magnetic fields;
(iii) addressing suitable and effective ways to synthesize both CNTs and graphene structures separately by parametric variation of a carbon arc.

This study presents a few significant insights on some of these issues through experiments on the magnetic field assisted electric arc and the corresponding product-analysis.

2. Experimental details

The experimental electric-arc reactor, with arrangements to superimpose an external magnetic field (symmetrically about the arc-axis) was designed and fabricated. After each operation, the as-synthesized carbon products were collected and thoroughly analysed with a number of characterizing tools. The following sections deal with the experimental methodology adopted for this purpose.

2.1. Description of the reactor

The schematic of the electrode assembly with an external steady non-uniform magnetic field is shown in figure 1(a). Here, the view of a vertical cross-section of this reactor along a plane passing through the axis of the reactor is shown. The main parts of this reactor consisted of two annular arrays of permanent ferrite magnets. The upper magnet array was aligned in a manner that all the south poles faced the axis of the array and all the north poles faced the bracket-axis for the magnets placed inside the lower bracket. The axes of these brackets were collinear with that of the main electrodes. Both
The magnet arrays were arranged in eight-fold symmetry about the reactor axis. The magnets were placed inside two annular brackets, made up of pure aluminium.

The separation ($\Delta Z$) between the lower face of the upper array and the upper face of the lower array, as shown in figure 1(a), could be manually adjusted with a precision of 1 mm. The magnet arrays could be moved symmetrically in the vertical direction with respect to the equatorial plane, as shown in figure 1(b). The anode was situated about 10 mm away from this equatorial plane as shown in the diagram. Due to the restrictions of the dimensions inside the chamber, the value of $\Delta Z$ could be varied from a minimum of 20 mm to a maximum of 80 mm.

The dimensions of the magnet assembly are provided in table 1. This geometrical distribution of the permanent magnets could generate magnetic lines of force distributed symmetrically about the axis of the arc (figure 1(a)) and could provide the means to vary the strength as well as the axial and radial field distribution by varying $\Delta Z$. Commercial ferrite magnets with a pole strength of 0.14 T having a Curie point of 170 $^\circ$C were used to produce the required magnetic field.

Water cooling was provided (flow rate $= 20$ lpm) with the help of a double-walled stainless steel (non-magnetic) jacket for maintaining the temperature of the magnets below their Curie point. The entire assembly was mounted inside the chamber, the details of which were provided in our earlier communication [22].

In the present magnet assembly, both the axial and the radial magnetic field strengths could be varied by changing $\Delta Z$. The strengths of both the axial and the radial magnetic field were measured by a Hall probe. The measured values are shown in figures 1(c) and (d). The magnetic field strengths, thus obtained, could regulate the strength of the Lorentz force, the description of which is provided in section 3.6.

| Specification                  | Value       |
|-------------------------------|-------------|
| 1 Dimension of the pole faces of the magnets | $25 \times 25$ mm$^2$ |
| 2 Width of each magnet        | 12 mm       |
| 3 Effective magnetic pole strength | 6.4 kG      |
| 4 Radial spacing between two consecutive magnet blocks in an array | 45 mm       |
| 5 Inner diameter of the magnet arrays | 90 mm       |
| 6 Outer diameter of the magnet arrays | 162 mm      |
| 7 Separation between the walls of the double-walled water cooling jacket | 10 mm       |
| 8 Accuracy of measuring $\Delta Z$ | 1 mm        |
| 9 Minimum value of $\Delta Z$ | 20 mm       |
| 10 Maximum value of $\Delta Z$ | 80 mm       |

Table 1. Dimensions of the magnet assembly.

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The components of the magnetic field were measured in the absence of the electrodes, arc and the water cooling jacket because of space constraints and the experimental convenience. The estimated values are presented in figures 1(c) and (d) to show the trend of their variation with $\Delta Z$. However, it was not possible to correctly estimate their actual values during the experiments at the location of the arc.

Table 2. Specifications of the experimental parameters.

| Parameter                     | Value  |
|-------------------------------|--------|
| Arc voltage                   | 22 V   |
| Arc current                   | 170 A  |
| Diameter of the anode         | 13 mm  |
| Diameter of the cathode       | 30 mm  |
| Operating pressure            | 500 Torr |
| Separation between the magnet arrays ($\Delta Z$) | 20–80 mm |
| Electrode composition         | 99.99% pure graphite |
| Buffer gas                    | 99.99% pure Ar |

2.2. Synthesis methodology

Initially, a base pressure of $10^{-3}$ Torr was obtained in the reactor chamber by an oil-rotary vacuum pump. The operating pressure in the reactor chamber was maintained at 500 Torr by making use of a throttle valve. The experiments were run at a steady arc current of 170 A (with a fluctuation of ±5 A) and an arc voltage of 22 V (with a fluctuation of ±2 V) in an atmosphere of 99.99% pure argon. The arc was struck in between two 99.99% pure and solid cylindrical glassy graphite (Graphite India Limited) rods with co-linear axes. One with 13 mm diameter served as the anode and was biased with the help of a current regulated power supply (6 kW capacity with an open circuit voltage of 60 V). The other electrode of 30 mm diameter was grounded and served the purpose of cathode. The orientations of these electrodes have been shown in figure 1(a).

The value of $\Delta Z$ was varied from 20 to 80 mm in steps of 10 mm. However, for maintaining a steady arc for all the values of $\Delta Z$, the arc voltage was carefully chosen to be fixed at 22 V. The operating conditions for this set of experiments are summarized in table 2.

After the completion of each synthesis run, the chamber was allowed to cool down to ambient temperature and the hard cylindrical deposits on the cathode surface were then dismantled for characterizations. The soft inner cores were not separated out and the cathode deposits (CDs) were characterized in their totality. After each synthesis run, the weight loss of the anode (with respect to its initial weight) and the corresponding weight of the CD were measured by a sensitive digital balance (100 g capacity with a least count of $10^{-4}$ g). After collection, the hard deposits were mechanically homogenized with the help of a pestle and mortar.

For the purpose of transmission electron microscopic (TEM) analysis, the powdered samples were thoroughly dispersed in N, N-dimethyl formamide [H·CO·N(CH$_3$)$_2$] for about 0.5 h. A small drop from each of these solutions, thus prepared, was then used for preparing the specimens on carbon coated copper grids. For the rest of the characterizations, the as-prepared powdered samples were employed with no further post synthesis treatment.

The TEM analysis was carried out by a 200 kV Tecnai G$^2$ 20 microscope, equipped with a LaB$_6$ filament and a CCD camera. Raman spectra were recorded in back-scattering geometry at room temperature with the help of a Jobin Yvon Labram HR800 spectrometer, in which a He–Ne laser ($\lambda = 632.81$ nm) was used for the Raman excitations. The integration time for recording the Raman spectra was 100 s and the spectra were averaged over three accumulations from...
the different parts of the same sample. The thermogravimetric (TG) analysis was carried out in flowing dry air ambience with a flow rate of $8.33 \times 10^{-7} \text{ m}^3\text{s}^{-1}$ by a 92-16.18 Setaram gravimeter at a temperature ramp of $5^\circ\text{C}\text{min}^{-1}$. For the TG analysis, the initial mass of each of the samples was taken to be about 8 mg.

3. Results and discussion

Initially, the arc was run under the conventional external magnetic field free conditions. The magnet arrays were removed from the water-cooled jacket and the arc was found to be nearly steady. However, on imposing the external magnetic field symmetrically (cylindrical symmetry) about the arc-axis, the arc was found to gyrate on the cathode surface uniformly. The extent of gyration increased with a decrease in the value of $\Delta Z$. At $\Delta Z = 20$ mm, the arc became unstable and got extinguished frequently. The data corresponding to $\Delta Z = 20$ mm were therefore deemed unreliable and not analysed in further detail.

The results revealed some of the new and interesting information on the mass of the CD, the evaporation from the anode, relative abundance of the various allotropic forms of carbon (including graphenes and CNTs) and Raman excitations due to the imposition of the external magnetic field.

3.1. Efficiency of formation of CD

The CD formed in a carbon arc is the only source of nanocrystalline structures of carbon comprising CNTs and CNPs [23]. The rest of the deposits, which are found outside the arc zone, are mostly amorphous carbon with traces of the members of the fullerene family. The percentage conversion ($\eta_{CD}$), of the consumed anode material into the CD, is therefore of practical importance for industrial production of nanocrystalline allotropes of carbon.

In the case of the present reactor, the chosen operating parameters resulted in an average anode erosion rate of about 500 mg min$^{-1}$. It was found that, in the absence of the magnetic field, about 90% of the consumed anode material was converted into CD. Figure 2 shows the variation of $\eta_{CD}$ as a function of $\Delta Z$. It is seen from this figure that, with a decrease in the value of $\Delta Z$ from 80 mm, the value of $\eta_{CD}$ decreases steadily reaching a minimum of about 55% at $\Delta Z = 60$ mm. With a further decrease in $\Delta Z$, the value of $\eta_{CD}$ is found to increase again, reaching a value of about 60% at $\Delta Z = 30$ mm.

Earlier work by us had demonstrated a value of $\eta_{CD}$ (optimum electric field conditions) close to the maximum obtained here [22, 24]. However, in the absence of any external field, the value of $\eta_{CD}$ was much less ($\sim 35\%$) with Ar–He and He–H$_2$ mixtures as buffer gases [22, 24]. When the buffer gas was changed to He, the value of $\eta_{CD}$ was found to be about 50% in the absence of the external magnetic field in the present reactor.

The data show that the value of $\eta_{CD}$ is greatly influenced by the nature of the buffer gas and the heat radiating systems. It seems that enveloping the arc with a heavier gas helps in achieving a better value of $\eta_{CD}$. This finding is extremely significant as it provides another control variable for the efficient synthesis of nanocrystalline carbon structures. Though this result is in accordance with the study reported in the literature [25], the exact mechanism of the arc, which governs the dependence of $\eta_{CD}$, is not understood well and can be further investigated in more detail in future scope of this work.

3.2. Variation of the diameter of CD

It was found that in the absence of the magnetic field, the diameter of CD ($\phi_{CD}$) was $\sim 14$ mm, which is very close to the diameter of the anode used. However, the value of $\phi_{CD}$ was found to be significantly affected in the presence of the external magnetic field. Figure 3 demonstrates the variation of $\phi_{CD}$ as a function of $\Delta Z$.

It is seen from this figure that, on decreasing $\Delta Z$ from 80 mm, $\phi_{CD}$ first steadily increases reaching a maximum of 20 mm at $\Delta Z = 60$ mm and then decreases steadily to a value of 15 mm at $\Delta Z = 30$ mm. This type of behaviour was not observed earlier [22, 24]. The increase in the value of $\phi_{CD}$ is a clear signature of the spatial expansion of the plasma plume by the magnetic field and a decrease in the same corresponds to the confinement of the CD formation zone.
3.3. Morphological analysis using TEM

Having observed the trend in figures 2 and 3, a few of the as-synthesized CDs were analysed by TEM in order to find out the morphologies of their constituents. Figure 4 highlights the typical TEM micrographs of the sample prepared in the absence of an external magnetic field. These TEM micrographs were recorded at different magnifications from different sites on the grid.

Figure 4 shows the presence of a large quantity of CNTs along with some CNPs with no traces of graphene-like structures. The diameter distribution of the CNTs is observed to be wide, ranging from 20 nm to more than 50 nm, and most of the CNTs are seen to form bundles. The wall-thickness of each of these CNTs is indicative of their multi-walled nature.

Distinct structural transformations of the constituents of the CD generated in the presence of the magnetic field were noticed in the corresponding TEM micrographs. Figure 5 shows some of the typical TEM micrographs of the sample generated at ΔZ = 60 mm.

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Figure 4. Typical transmission electron micrographs of the sample synthesized under zero magnetic field condition.

In order to investigate the graphene-like structures, synthesized at ΔZ = 60 mm in more detail, selected area electron diffraction (SAED) patterns were recorded from typically two circular regions, which are labelled by 1 and 2 in figure 5.

In figure 5, the circles labelled 1 correspond to the typical SAED pattern, which is shown in figure 6(a), while the circles labelled 2 correspond to the typical SAED pattern as shown in figure 6(b).

The difference between these two SAED patterns is clearly visible. The characteristic features of the SAED pattern in figure 6(a) are the presence of circular rings along with some symmetric bright spots. The rings correspond to the (h k 0) type reflections of graphite and the bright spots correspond to the lattice spacing of the (00l) planes of graphite. The streaks of the intensity radiating outwards and parallel to [0 0 l] from the (h k 0) type rings confirm the [14] independent scattering from the delaminated curled graphitic sheets. These features of the electron diffraction pattern correspond to a typical electron diffraction taken perpendicular to a CNT, as reported in the literature [14].

On the other hand, the SAED pattern in figure 6(b) is seen to comprise oval shaped rings. In electron diffraction experiments we are usually accustomed to observing circular Debye rings. The occurrence of oval shaped nearly continuous rings is therefore a bit unusual. After measuring along the minor axes of the oval shaped rings, as indicated by arrows,
we could successfully correlate these rings with the \((h k 0)\) reflections \((100), (110), (200), (210)\) and \((300)\). The shape of the Debye rings from the powder samples is exactly circular, because, it appears as an intersection of the Ewald plane with the sphere of reflection in the reciprocal space. Thus, concentric oval shaped diffraction rings will appear when the Ewald-plane intersects coaxial hollow cylinders of reflections in the reciprocal space. It is very obvious from the diffraction results that only the \((h k 0)\) type reciprocal lattice points of graphite have got extended in the reciprocal space.

Figure 5. Typical transmission electron micrographs of the sample corresponding to \(\Delta Z = 60\) mm.

Figure 6. (a) Typical SAED pattern obtained from an area shown by circles labelled by 1 in figure 5 and (b) the pattern obtained from the circles labelled by 2 in the same figure.
This extension is measured to be roughly $\sim 0.5 \text{ Å}^{-1}$. This could be calculated taking into consideration the difference between the lengths of the semi major and semi minor axes of the oval shaped diffraction patterns. Such a large 1D extension in reciprocal space directly implies that the layers of graphite have got delaminated to a thickness of a few atomic orders, i.e. the corresponding diffraction pattern corresponds to graphene sheets. The lateral extents of these sheets are large. The presence of the nearly continuous nature of oval rings dictates that the $(h k 0)$ graphitic sheets are randomly oriented about an axis perpendicular to them.

Figure 7 shows typical TEM micrographs corresponding to $\Delta Z = 30 \text{ mm}$. Distorted carbon structures, other than CNTs and graphenes, are easily noticeable in each of these micrographs. The majority of the constituents of the corresponding CD seem to be the CNPs along with traces of a few CNTs.

Analysing figures 6 and 7 carefully, it is inferred that the external magnetic field, as has been used in this study, does not help in the formation of CNTs in an arc process. It stops the growth of CNTs and helps in the formation of graphene-like structures. In other words, one can infer that the directional motions of the carbon precursors, which are thought to be responsible for the growth of CNTs [22] in the arc, are hampered in the presence of an external magnetic field. The situation rather promotes the formation of 2D graphene structures in an arc process.

3.4. Thermogravimetric analysis

The oxidation behaviour of the CDs is another important property and gives information about their crystalline purity and composition. While carrying out the TGA measurements, it was found that none of the samples underwent any weight loss before 500°C. In order to get better accuracy and resolution, TGA measurements, therefore, were carried out from 500 to 1000°C. Figure 8 summarizes the outcomes of this study. For comparing the data generated in the presence of the magnetic field to those generated in the absence of the magnetic field on the same graph, an asymptotic point $\Delta Z = \infty$ has been incorporated equivalent to the condition $B = 0$ in this figure. In the first column of figure 8, the percentage weight loss (TG) of the samples as a function of temperature for different values of $\Delta Z$ is shown. The initial weight of the starting material is considered to be 100%. It is seen that, as the sample temperature is increased beyond 500°C, most of the samples start to reduce their weight. This weight loss is accounted for the formation of CO (g) and CO$_2$ (g) as a result of the oxidation of the samples by the O$_2$ molecules present in the oxidizing air.

However, in order to understand the nature of oxidation for different samples in more detail, derivatives of the TG (DTG) curves were obtained. The DTG curves are shown in the second column of figure 8 for different values of $\Delta Z$. It is clearly seen from these curves that oxidation behaviour is quite different from sample to sample. The oxidation of none of the samples, under investigation, is seen to be a single step process. This indicates that the samples undergoing oxidation are not composed of a single carbon allotrope. Rather, deconvolution of the DTG curves into a number of Lorentzian line shapes, in order to obtain the best fitting to the experimentally obtained DTG curves, clearly reveals the presence of a variety of components in different weight proportions. It is difficult to identify ‘each and every’ specie corresponding to each
Figure 8. Oxidation behaviours of the composition of CD synthesized at different values of \( \Delta Z \) along with the one synthesized under no external magnetic field condition. In the DTG curves, the Lorentzian line shapes and the overall fittings are shown.
value of $\Delta Z$ due to the lack of exact knowledge of all these carbonaceous species.

However, oxidation temperatures of different carbonaceous species along with their contributions in weight percentage in each sample could be calculated with the help of the areas under the corresponding Lorentzian line shapes. The results of these calculations are shown in the third column of figure 8. The distribution of oxidation temperatures and corresponding percentage weight contributions of different carbonaceous species as a function of $\Delta Z$ shows irregular behaviour. This kind of fluctuation may best be attributed to the arc irregularities [26].

The major impacts of the external magnetic field could be recognized, while looking at the most probable oxidation temperature ($T_P$) of different samples as a function of $\Delta Z$. $T_P$s were estimated from the DTG curves in figure 8 and correspond to the maximum amplitude of the associated curves. It is calculated that the sample prepared in the absence of the external magnetic field exhibits the highest value of $T_P$ (829 °C). The variation of $T_P$ as a function of $\Delta Z$ is presented in figure 9. Though $T_P$ did not show much variation in the range of 40 mm $\leq \Delta Z \leq$ 80 mm, a closer look at figure 9 shows that, in this range of $\Delta Z$, there is a local minimum of $T_P$ (767 °C) at $\Delta Z = 60$ mm. The TG spectrum for each sample was recorded thrice and the corresponding $T_P$ was not found to fluctuate beyond ±2 °C. Moreover, the powdered CD generated at $\Delta Z = 30$ mm exhibited the lowest value of $T_P$ (690 °C) among all the CDs synthesized in the presence or absence of the external magnetic field.

3.5. Raman spectroscopic analysis

Raman spectroscopic (RS) analysis is a very powerful tool to infer the structural morphologies of different carbonaceous samples. It distinguishes the graphene structures from the other carbon structures and can provide significant information about the relative defect concentration and finite size effects in an unknown carbonaceous sample [27].

RS measurements were carried out in a slightly non-conventional way in the case of this work. Not only was the overall quality of each sample analysed by this tool, but the CDs were also analysed separately in more detail.

Firstly, for recording the Raman spectra, circular slices of about 5 mm thickness were skillfully cut from each CD synthesized under different values of $\Delta Z$. Of these slices, three different portions were analysed by RS. These positions were: (i) the centre of the CD, (ii) at the $R/2$ position of the CD, where $R$ is the radius of the soft black core of the CD and (iii) at the edge of the soft black core of the CD, as shown in figure 10. At least three different measurements were carried out for each of these three positions to identify the average features. A laser beam with a spot diameter of 1 $\mu$m was used for this purpose.

In all the cases, Raman spectra were recorded in the range 100–1800 cm$^{-1}$. However, no peak was identified in the lower range (100–1100 cm$^{-1}$) of the Raman spectra. These spectra exhibited the presence of only two distinct peaks, which could be identified as the D and G bands [27]. A typical such spectrum is shown in figure 11. Common features in all these Raman spectra are the three peaks. One, at around 1340 cm$^{-1}$, is correlated with the so-called disorder induced D band, and the other at around 1580 cm$^{-1}$, is referred to as the G band associated with a shoulder at 1620 cm$^{-1}$ [27]. To facilitate quantitative estimates, the relative intensities of G and D bands have been determined from the areas under the corresponding peaks. For enabling a proper comparison, all the G band amplitudes were normalized to unity. The G band intensities were determined after deconvoluting the G bands into two Lorentzians and then considering the areas only of the Lorentzians centred at 1580 cm$^{-1}$, as discussed in our earlier
reports [22, 24]. \( I_G \) and \( I_D \) are the areas under the peaks at 1580 cm\(^{-1}\) and 1330 cm\(^{-1}\), respectively.

The \( I_G/I_D \) ratio was then calculated and plotted for the three different positions of the CDs generated under the different values of \( \Delta Z \), as shown in figure 12.

It was found that in the absence of the external magnetic field, the \( I_G/I_D \) ratio exhibited a maximum of 16 at the centre of the corresponding CD and its value steadily decreased to a value of 6 on moving towards the edge of the CD. On the other hand, the ‘maxima’ of this ratio are seen to shift towards the edge of the CD generated in the presence of the external magnetic field (figure 12).

The G band arises due to in-plane vibrations of the hexagonal graphene-like structures [27]. The broad shoulder centred at around 1340 cm\(^{-1}\) (D band) has been extensively studied and has been explained by the relaxation or breakdown of the wave vector selection rules due to the finite size of the crystals in the bulk material [28], and a peak in the Raman spectra occurs near the maxima in the phonon density of states. In the case of our samples, the D band corresponds either to the CNPs due to their finite size or to the structural defects in the carbon nanostructures, the relaxation of wave vector being equally valid for both.

The \( I_G/I_D \) ratio is a well-accepted index for analysing the fractional content of the ordered graphene structured species within a carbonaceous sample and an increase in this ratio indicates an increase in the graphene structured species and a decrease in the defect density, relative number of CNPs and percentage of a-C content [24].

The variation of the \( I_G/I_D \) ratio for a magnetic field free arc is a clear indication of the fact that the central part of a conventional carbon arc is rich in graphene structured species. This is consistent with the fact that CNTs are formed at the central part of the CD, thereby enhancing the overall graphene structured contents on account of the maximum local arc temperature at this position [23]. On moving towards the edge of the CD, there is a gradual decrease in the local arc temperature, which promotes the formation of less graphitized species.

However, figure 12 reveals that, on imposing the external magnetic field, the extent of graphitization shifts towards the periphery of the soft black inner core of the CD for 80 mm \( \leq \Delta Z \leq 60 \) mm. On decreasing the value of \( \Delta Z \) below 60 mm (increase in the radial magnetic field), the extent of graphitization again increases and shifts towards the \( R/2 \) position of the CD. It is also equally noteworthy that the \( I_G/I_D \) ratio remains almost equal at the centre and the \( R/2 \) positions of the CDs corresponding to 80 mm \( \leq \Delta Z \leq 60 \) mm. This observation is a clear signature of the homogenization of the radial distribution of the local arc temperature possibly due to rotation of the arc column due to the imposed magnetic field. It is also noteworthy that the nanostructures generated near the axial region of the arc, in the presence of the external magnetic field, are always less graphitized than those generated away from the arc-axis. This trend is exactly opposite to that observed under no magnetic field condition.

Following these measurements, in order to check the overall quality of each sample, all the CDs were crushed thoroughly and Raman measurements were carried out again for these powdered samples.

The first column of figure 13 shows the first order Raman spectra recorded in the range 1100–1700 cm\(^{-1}\) for the mechanically homogenized CDs generated at different values of \( \Delta Z \). The presence of both the D and the G bands is clearly seen in this figure. The asymptotic point \( \Delta Z = \infty \) in this figure has the same meaning as in figure 8.

Figure 14 shows the variation of the \( I_G/I_D \) ratio as a function of \( \Delta Z \).

It is noteworthy that the carbonaceous sample corresponding to no magnetic field condition exhibited the highest value of the \( I_G/I_D \) ratio with \( I_G/I_D = 14 \). However, the point corresponding to \( \Delta Z = 60 \) mm also exhibits a distinct maximum with \( I_G/I_D = 10 \) among all the samples synthesized in the presence of the external magnetic field (figure 14). The trend of the variation of the \( I_G/I_D \) ratio with \( \Delta Z \) is very similar to that seen in the variation of the diameter of the CDs (figure 3).

From the values of the \( I_G/I_D \) ratio, it is logical to infer that the sample synthesized under no external magnetic field condition has the highest degree of graphitization and contains the least number of structural defects. On imposing the external magnetic field, the extent of graphitization decreases. However, the sample synthesized at \( \Delta Z = 60 \) mm is definitely richest in terms of the graphene structured contents among all the samples synthesized in the presence of the external magnetic field.

It is worth mentioning that an extensive analysis of graphenes has been reported by Ferrari et al [29], who have demonstrated that the second order Raman peak centred at 2700 cm\(^{-1}\) (2D peak) is the characteristic graphene feature and can be very useful in identifying the number of layers in a few-layer graphene sample. However, a later inspection of this peak for our samples did not provide any useful information for the in-depth analysis of the as-synthesized graphenes. As all the as-synthesized samples are composed of various allotropic forms of carbon, present in different proportions, the corresponding 2D peaks could not provide information only of the graphene structured contents. It is therefore felt necessary...
Figure 13. The first column shows the first order Raman spectra of the mechanically homogenized CDs synthesized under different values of $\Delta Z$ along with the one corresponding to no external magnetic field. The second column shows the deconvolutions of the G bands into two Lorentzian line shapes.
to isolate the graphene structures from the as-synthesized samples first before their in-depth analysis can be carried out using Raman spectroscopy following the work of Ferrari et al [29]. This further analysis is proposed to be carried out along with the one corresponding to no external magnetic field.

In summary, the results have clearly revealed that:

(i) The CD generated in the absence of an external magnetic field exhibited a high $I_G/I_D$ ratio of 14 in the Raman spectra. The corresponding most probable oxidation temperature was found to be quite high (829 °C) (figure 13). These features support the fact that the corresponding CD is rich in MWNTs (figure 4).

(ii) An arc-plasma, under the action of a specially configured magnetic field, helps in the formation of graphene-sheet-like structures. The CD generated at $\Delta Z = 60\text{ mm}$ exhibited a relatively high oxidation temperature (767 °C) and it was found to be a rich source of graphene-sheet-like structures (figures 5 and 13). On the other hand, from figures 7 and 13 it is seen that the CD synthesized at $\Delta Z = 30\text{ mm}$ was rich in CNPs and showed a relatively low oxidation temperature (690 °C). The graphene-sheet-like structures can be viewed as metastable or intermediate forms of CNT-growth. These sheets are highly graphitized and are expected to burn at lower oxidation temperature than CNTs and CNPs, which are known as the stable structures of carbon. However, on account of the observed higher oxidation temperature of the CD, rich in these sheets, with respect to the one rich in CNPs, it is possible that, while recording the TG spectra of the corresponding CDs, these sheets first roll up to minimize their surface energy and then get oxidized.

The behaviour observed below the optimum magnetic ring separation ($\Delta Z = 60\text{ mm}$) is not well understood. The corresponding CDs are found to be composed of mostly CNPs along with some traces of CNTs (figure 7). This might be due to plasma instability on account of the imposition of the magnetic field with high strength.

A clear understanding of this behaviour has not been achieved. However, an attempt at understanding the behaviour of arc in the presence of the used magnetic field assembly is made in the following section.

3.6. Behaviour of electric arc in the presence of the magnet assembly

An electric-arc column at a pressure of 500 Torr behaves like a pure electrical conductor. As the charged plasma precursors are in a high-collision regime, the effects of the external magnetic field will not be on individual precursors; rather the magnetic field will modulate the entire arc column. A typical nature of the magnetic field produced near the arc zone in this case has been schematically shown in figure 1. It has also been found that a magnetic field generated by the magnet arrays is not perfectly axial. The magnetic field vectors thus generated can best be described as

$$\mathbf{B}(\rho, z, \Delta z) = B_\rho(\rho, z, \Delta z)\hat{\rho} + (-B_\rho(\rho, z, \Delta z))\hat{\rho}.$$  \hspace{1cm} (1)$$

taking into consideration the cylindrical symmetry of the arc. Here, $B_\rho$ and $B_z$ are the axial and radial components of the magnetic field respectively. The drift velocity of the plasma precursors can be expressed as

$$\mathbf{V}_d = V_z(\rho, \Delta z)\hat{z} + V_\rho(\rho, \Delta z)\hat{\rho}.$$  \hspace{1cm} (2)$$

for the present case. $V_\rho$ will always be positive, because the dimension of the cathode is larger than that of the anode in the present case. As a result, the Lorentz force acting on a charged particle will take the form

$$\mathbf{F}_{\text{Lorentz}} = q \times (\mathbf{V}_d \times \mathbf{B}(\rho, z, \Delta z))$$

$$= q [(V_z(\rho, \Delta z)B_\rho(\rho, z, \Delta z) - V_\rho(\rho, \Delta z)B_z(\rho, z, \Delta z))]\hat{\phi} + (J_z(\rho, \Delta z)B_\rho(\rho, z, \Delta z) - J_\rho(\rho, z, \Delta z)B_z(\rho, z, \Delta Z))]\hat{\phi}.$$  \hspace{1cm} (3)$$

making use of equations (1) and (2). Here, $q$ is the charge of the plasma precursor and $\mathbf{J}$ is the current density. For a current carrying plasma column, equation (3) would describe the net $J \times \mathbf{B}$ force. Hence, depending on the magnitude of the Lorentz force, the entire current conducting channel of the arc will gyrate in the $\pm \phi$ direction with different rotational frequencies following equation (3).

The dynamics of the arc column is decided by the magnitudes of $J_\rho$, $J_z$, $B_\rho$ and $B_z$ on the cathode and anode surfaces. As the current distribution at the cathode and anode surfaces will critically depend on the surface-geometry of both the anode and the CD, they would decide the relative magnitudes of $J_\rho$ and $J_z$. At high values of $\Delta Z$; the magnetic field at the cathode is mostly axial (figures 1(c), (d)). In the full range of $\Delta Z$, in the experiment, the ratio of the axial to the radial field varied between 0 and 100 at $r = 10\text{ mm}$, where $r$ is the radial distance close to the cathode surface (figure 1). Therefore, the net force would critically depend on $J_\rho$ and $J_z$ at the cathode.

As seen from the data on the estimated CD diameter (figure 3), $\Delta Z = 60\text{ mm}$ gives the maximum size of 20 mm. The diameter reduces as $\Delta Z$ is reduced below 60 mm and

![Figure 14](image-url)
remains more or less constant below 40 mm. Similarly, the RS data indicated increased presence of graphene structured species at the periphery at $\Delta Z = 60$ mm, whereas $\Delta Z = 40$ shows maximum graphene structures at $r = R/2$ and $\Delta Z = 30$ shows a high quantity of the graphene structured species again at the periphery. The thermogravimetry data indicated a monotonic decrease in the most probable oxidation temperature, with a local minimum at $\Delta Z = 60$ mm, as the magnetic field increased. On the other hand, the TEM features (figures 4, 5 and 7) of the CD compositions show transitions from CNPs to CNTs through graphene sheets formation on gradually withdrawing the external magnetic field.

As a result of the Lorentz force, the arc column will rotate about the axis of the electrodes and the cathode spot will decentralize and anchor towards the periphery of the cathode. In consequence of this, the local arc temperature of the arc will be more towards the periphery of the CD than at its central zone. The local graphitization will therefore be more towards the periphery of the CD. The more the Lorentz force, the more will be the extent of decentralization of the graphitizing zone. In view of this fact, it seems that the arc rotation is maximum at $\Delta Z = 60$ mm and decreases gradually on deviating from this condition. Figure 3 provides strong support for this conjecture.

Though it is extremely difficult to reconcile all the observed data through arc dynamics without detailed measurements of current density distribution, magnetic fields and associated simulation, $\Delta Z = 60$ mm indicates a situation conducive to the enhanced formation of few-layer graphene sheets. A few remarks to explain the observed trend can be made as follows.

At first glance, the rotation of the arc column and the relative magnitude of the two competing terms $J_\rho B_z$ versus $J_\phi B_z$ appear to be responsible for the described behaviour. This is further supported by the fact that graphitization is possible only at high temperature of the cathode surface. Possibly, at $\Delta Z = 60$ mm, the conditions are most favourable for the rotating arc column to cover a major area of the cathode. As $\Delta Z$ is decreased further, beyond 60 mm, the force balance (equation (3)) changes and the graphitization as well as the CD shrink towards the axis.

However, this simplistic scenario needs to be supported by detailed quantitative measurements and simulation of the current density vectors, plasma column diameter and speed of arc rotation. That is outside the scope of this work and can be considered for future work.

4. Conclusions

The study of magnetic field assisted synthesis of carbon nanostructures in a carbon arc has resulted in extremely interesting data not reported in the literature so far. It has been shown that arc electric field and steady non-uniform magnetic field can influence the precursor trajectories and energies to effect stacking of carbon atoms promoting the growth of CNTs or graphene-sheet-like structures. The conclusions drawn from this study can be summarized as follows.

It seems that the growth of carbon nanostructures takes place near the cathode surface. The nature of the growth is decided by the directions of movements of the carbon precursors reaching the cathode surface. The directional motions of the carbon precursors along the electrodes’ axis, in a conventional arc, are responsible for the growth of CNTs [22]. However, an arc, rotating on account of an external magnetic field, favours stacking of carbon precursors preferably along the surface of the cathode, assisting in the formation of graphene-sheet-like structures.

However, the most significant contribution of this paper is to unfold a novel physical route, which is capable of producing large quantities of few-layer graphenes at a much faster rate directly from the gas phase condensation of carbon precursors in an electric-arc method. The attempt is the first of its kind and is envisioned to attract more physicists to contribute significantly in the field of graphene monolayer synthesis, which is rather the choice of chemists at present [30].

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