The efflorescent carbon allotropes: fractality preserved blooming through alkali treatment and exfoliation

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Abstract
The work reported in the paper elucidates morphological modification induced nanoart and surface area enhancement of graphite, graphene, and soot containing carbon allotropes through ultrasonication and alkali-treatment. The field emission scanning electron microscopic (FESEM) analysis of the samples before and after exfoliation reveals the formation of brilliant flower-like structures from spindle-like basic units due to Ostwald ripening. The x-ray diffraction analysis of the samples gives information about structural composition. The fractal analysis of the FESEM images indicates a multifractal structure with the dimensions—box-counting dimension $D_0$ (1.72), information dimension $D_1$ (1.66), and correlation dimension $D_2$ (1.63)—preserved upon exfoliation. The process of ultra-sonication assisted liquid phase exfoliation resembles blooming as if the carbon allotropes are efflorescent.

1. Introduction

Innovations in tuning the properties of technologically significant materials is a crucial area of research in Nanotechnology. It provides greater flexibility and advantage of synthesising efficient nanostructured materials for the design of new functional devices by controlling its size and morphology. The nanomaterials exhibiting precise morphologies find immense applications in energy storage devices, bleaching agents, drug delivery, gas sensing, optical storage devices, and catalysis [1–3]. The tailored morphologies of nanomaterials show excellent physical, chemical, electrical, optical, thermal, and magnetic properties that attract the researchers in this field. There exists a variety of experimental methods like co-precipitation, sol-gel, spray-pyrolysis, exfoliation, hydro- and solvothermal, for the fabrication of nanoscale materials with diverse morphologies [1, 4]. Among them, the simplest one is the liquid-phase exfoliation (LPE), where the layers of the materials are separated by suitable techniques [5]. The ultra sonication-assisted LPE (ULPE) is a widely used synthesis route for preparing high-quality crystalline graphene sheets [6, 7].

Carbon is one of the wealthiest resources on earth that exists in different allotropic forms with distinct physicochemical properties. Zero dimensional fullerenes, one-dimensional carbon nanotubes, two-dimensional graphene, and three-dimensional graphite are some of the primary allotropic forms of carbon with immense applications in all fields of science and technology, which reveals the significance of morphology tuning [8, 9]. Soot particles formed as a by-product of incomplete combustion is a store-house of various allotropes of carbon. The burning of any kind of hydrocarbons like ring-structured camphor, long-chain fatty acid-containing oils, the engine fuels—petrol and diesel, can produce the futile soot containing carbon nanoparticles [10–13]. If these waste soot nanoparticles can be effectively utilised for fruitful applications by tuning its morphology, it could be beneficial to the society as well as the environment. The carbon nanoparticles with varied morphologies can easily be synthesised by the sonication-assisted LPE method, as it involves the proper selection of a solvent and secondary agent (organic and inorganic salts, use of surfactants, or by increasing the sonication time). Even though water is a good dispersion solvent in many of the exfoliating processes [5, 14], the use of volatile solvents with low boiling points (acetone, chloroform, isopropl alcohol, and ethanol) are preferred [15, 16] because it enables more manageable recovery of the material, by simple air-drying, without the formation of any unnecessary chemical
compounds. The criteria for the selection of secondary agents are the availability, non-toxicity, and cheap chemicals. Hence, sodium hydroxide (NaOH) is a better choice compared with the commonly used sodium lauryl sulfate, cetrimonium bromide, phenolphthalein, and anthracene [17]. It is also well-reported in the literature that the addition of a small amount of NaOH can enhance the yield of the exfoliated graphene from graphite. The exfoliation happens because of the intercalation of NaOH into the graphitic layers, weakening the van der Waals' force, and thereby expanding the interplanar spaces between the layers [6]. Thus, the separation of layers help in the formation of nanostructures of morphologies with larger surface area [5]. The present work is an attempt to tune the morphology of the soot containing carbon allotropes, graphite, and graphene, using simple ULPE method and also to study the fractality.

The concept of infinitely complex, self-similar patterns, seen from microcosm to macrocosm, termed fractals, are introduced by the famous fractalist B. Mandelbrot [18, 19]. The nanoclusters of chemically identical particles in the fluid are fractals, and they are expressed by the non-integer fractal dimension (D) [20, 21]. The fractal analysis has become an imperative analytical tool in the various realm of arts, science, social science, and technology. Box-counting, power spectrum, walking divider, and area-based methods are some among the commonly used methods for finding the value of D. The widely used differential box-counting (DBC) method popularised by N Sarkar et al [22] is considered as the practically reliable method for the estimation of D for grayscale images, which is based on the intensity variations in the images. Many of the natural and experimental phenomena are complex, that requires a spectrum of generalised dimensions/multifractals for detailing the system completely. The multifractal analysis is a sensitive tool often used for analysing the growth and aggregation of nanoparticles. The multifractals can be wholly characterised with multiple scaling rules or dimensions such as box-counting, information, and correlation dimension [23, 24]. The beautiful morphologies, produced as a result of alkali-treatment and sonication-mediated LPE, of the graphite, graphene, and soot containing carbon allotropes are subjected to multifractal analysis for understanding the fractal dimension of the morphology of the allotropes before and after exfoliation.

2. Materials and methods

The possibility of morphology tuning using exfoliation and alkali treatment is carried out in graphite, graphene, and soot containing carbon allotropes. The soot particles are collected from the petrol and diesel internal combustion engines and by burning the natural hydrocarbon source, camphor. The soot is washed in double-distilled water several times to remove the impurities, dried in an air oven for 3 h, and powdered [10–13]. Two commercially available carbon allotropes, graphite and graphene, are also subjected to exfoliation study. In the present LPE method, the ethanol–water mixture (ratio: 1:1) is used as the solvent and NaOH as the secondary agent. 1.5 mg of carbon nanoparticles—graphene (Rb), graphite (Gb), petrol (Pb), diesel (Db), and camphor (Cb) soot—are dispersed in the solvent, followed by addition of NaOH (3 mg). This mixture is then ultra-sonicated in LMVC series Ultra-sonicator for one hour, at a constant temperature at 30 °C to obtain nanostructures with varied morphologies. The exfoliated and alkali-treated samples are labelled as graphene (Rb), graphite (Gb), petrol (Pb), diesel (Db), and camphor (Cb) soot. The suffixes a and b in the labels indicate after and before LPE, respectively. The samples are drop cast in a silica wafer, dried and subjected to structural and morphological characterisations by x-ray diffraction (XRD- Bruker D8 Advanced Diffractometer with CuKα radiation with λ = 1.5406 Å) and Field Emission Scanning Electron Microscopic (FESEM- Nova Nano) analyses.

The electron microscopic images of the samples before and after LPE and alkali-treatment are subjected to multifractal analysis for understanding the fractal structure. The multifractal analysis is carried out using ImageJ—Fraclac software. The most suitable method for finding the multifractal dimension of grey value images is by differential box-counting. It is based on the differences in the maximum and minimum intensity values in a box having a particular box-size. The generalised dimension D(q), which indicates the variation in mass or pixels per box with box sizes/resolution, quantifies the multifractal nature of an object. In other words, when an arbitrary range of values q, also called the probability moment, distorts a system, the variation in its probability distribution is obtained through D(q) [23, 24]. If Pq(ε) and Mq(ε) denotes the grey value distribution probability and grey value of the box (i, j) with box size ε, then the probability distribution of each box is obtained from the equation (1)

\[
P_q(\varepsilon) = \frac{M_q(\varepsilon)}{\sum_{i,j=1}^{N} M_{ij}(\varepsilon)}
\]
In terms of $P_i(\varepsilon)$, the distorted probability distribution $(I(q, \varepsilon))$ is expressed as equation (2)

$$I(q, \varepsilon) = \sum_{i,j=1}^{N} [P_{i,j}(\varepsilon)]^q$$  \hspace{1cm} (2)

The generalised dimension $D(q)$ is obtained from the relation (equation (3))

$$D(q) = \lim_{\varepsilon \to 0} \frac{\ln I(q, \varepsilon)}{\ln \varepsilon^{-1}} / [1 - q]$$ \hspace{1cm} (3)

Different values of $q$ give different kinds of information about the system. For $q = 0$, global knowledge about the fractal object can be obtained through the capacity/box-counting ($D_0$) dimension that is independent of the probability moment. The information dimension ($D_1$), which denotes the degree of disorder of the system through the density distribution of points, is obtained for $q = 1$. For the generalised dimension with $q = 2$, we get the correlation dimension ($D_2$), giving details regarding the degree of correlation among the neighbouring data. It is defined that a function of monofractal/non-fractal object is a linear straight line, whereas that of a multifractal object is sigmoidal or decreasing [24].

3. Results and discussion

In the present work, the samples are subjected to structural and morphological characterisations by XRD and FESEM. Figure 1 displays the XRD pattern of the samples used in the present investigation before exfoliation. The amorphous nature of the samples is evident from the broad XRD pattern of samples $R_b$, $P_b$, $D_b$, and $C_b$ in the 2theta range 20°–30°. The contribution of the amorphous content/defects in the sample is understood from the peak at 20° corresponding to the (002) plane [12]. The sample $G_b$ shows a crystalline peak at 26°, indicating the characteristic graphitic peak. We have reported that camphor soot is rich in CNTs as evidenced through the peaks at 25° and 42° and also that the diesel soot is rich in graphene [10, 12]. The XRD pattern of the samples

![Figure 1. XRD pattern of—$G_b$—camphor soot, $D_b$—diesel soot, $P_b$—petrol soot, $G_b$—graphite, and $R_b$—graphene.](image)
shown in Figure 1 is in good agreement with our earlier reported observation, confirming the presence of carbon allotropes in soot in varying amount. The broad peak at 42°, which is a prominent peak indicating the graphitic carbon, is present in all the samples [11, 12].

FESEM helps in visualising topographic details of the sample at the nanoscale. The FESEM images recorded at two different scales, micrometre and nanometer, give a better understanding of the morphology. A closer examination of these images reveals the agglomeration of the spherical primary structures that are held together through the weak Van der Waals force of attraction. The binding and orientation of these primary structures forming the carbon nanoparticles (CNPs), in the soot, graphene, and graphite, give rise to different morphologies. The weak Van der Waals force of attraction existing between them permits reorientation or separation of the basic units through ultrasonication and chemical treatment. In the present study, the samples—camphor soot, diesel soot, petrol soot, graphite, and graphene—are ultrasonicated for 1 h in the ethanol-water mixture with NaOH as the secondary agent. The morphological modifications, before and after alkali-treatment and ultra-sonication, are recorded using FESEM and are shown in Figures 2–6.

The FESEM image of camphor soot shown in Figures 2(a) and (b) show spherical CNPs of size between 30–60 nm linked together to form a chain. The exfoliation brings about drastic modifications in morphology as evidenced by Figures 2(c) and (d), which shows spherical CNPs attached to the ends of rod-like structures. A close-up of the image shown in the inset of Figure 2(c) indicates a spindle-like structure (of length 1.15 μm) as the basic building block and resembles a flowering plant or efflorescent soot. From literature, it can be seen that camphor soot is rich in CNT content. The observed nanorods in Figure 2(d) may be due to the bundling of CNTs with the CNPs attached together. In one of our earlier work, we have shown the presence of CNTs and CNPs in camphor soot and its thermal-induced modifications [12]. The formation of nanorods from spindle-like structures can be attributed to Ostwald ripening [5, 25]. The NaOH acts as a facilitator in the exfoliation process, the mechanism of which can be explained as the intercalation of Na⁺ and OH⁻ ions into the interplaner spaces of the allotropes to be exfoliated.

The morphological modification of the diesel soot from agglomerated spherical CNPs to marigold flower-like structures due to the alkali treatment and sonication is evident from Figures 3(a)–(d). The agglomerated soot nanoparticles of size 30–40 nm can be seen in Figures 3(a) and (b), whereas the flower-like formation can be seen after exfoliation (Figures 3(c) and (d)). When the image of the exfoliated sample is further zoomed out, spherical CNPs attached to the petal-like structure can also be seen. Here also, the formation of flower-like structure is due to the Ostwald ripening of the basic units. Investigations with petrol soot also found to yield brilliant morphologies upon ULPE as shown in Figure 4. The agglomerated structure (Figures 4(a) and (b)), turns into
structures resembling half-bloomed jasmine flowers (figures 4(c) and (d)). Thus the futile soot containing varied allotropes of carbon can be tailored into beautiful flower-like structures of greater surface area making them suitable for surface-area dependent applications in electronics, bleaching, and catalysis.
The graphite is another allotrope form of carbon that finds applications in nanoelectronics. The exfoliation of flake-like graphitic structures (figures 5(a) and (b)) also results in floral patterns and beautiful bouquet-like structures, as shown in figures 5(c) and (d). The observation of exfoliated sample reveals the

![Figure 5. FESEM images of graphite—(a) and (b) before exfoliation; (c) and (d) after exfoliation.](image)

![Figure 6. FESEM images of graphene—(a) and (b) before exfoliation; (c) and (d) after exfoliation.](image)
formation of flower-like structures from spindle-like units attached to rod-like structures. The highly porous and layered structure of graphene nanosheets are broken into highly disordered thinner teared petal-like structure on alkali treatment and exfoliation, which is visible from figures 6(a)–(d). Though brilliant floral patterns could be developed, effective surface area enhancement is achieved upon exfoliation. The study suggests that the alkali treatment and exfoliation turn the soot as an efﬂorescent carbon allotrope.

From the FESEM analysis of the graphite, graphene, and soot containing carbon allotropes before and after alkali-treatment and ULPE, it is obvious that the tuning of morphology into beautiful flower-like structures is possible. From literature, it can be seen that the fractal analysis can be employed as a surrogate technique for FESEM analysis [26]. For understanding the fractal structure and computing the fractal dimension, various portions of the greyscale FESEM images of the samples before and after alkali-treatment and ULPE are subjected to multifractal analysis by differential box-counting method. The multifractal spectrum, obtained by plotting $D(q)$ versus $q$, shows a sigmoidal nature giving three dimensions—$D_0$ ($q = 0$), $D_1$ ($q = 1$), and $D_2$ ($q = 2$). A representative multifractal plot of $D(q)$ versus $q$ is shown in figure 7(a) and the whisker-and-boxplot of the values of dimensions, $D_0$, $D_1$, and $D_2$ are shown in figures 7(b)–(d), respectively. The values of dimensions ($D_0$, $D_1$, and $D_2$) of all the samples ($R_b$, $G_b$, $P_b$, $D_b$, and $C_b$) are put together in the same whisker-and-boxplot as their values are close together. The whisker-and-boxplots are also drawn for the samples after exfoliation ($R_a$, $G_a$, $P_a$, $D_a$, and $C_a$). The $D_0$ of the fractal image before and after exfoliation are found to be around 1.72, which gives information about the complexity of the image. The nearly same value of $D_0$ before and after exfoliation suggests that the complexity at the microstate remains unchanged despite morphological modifications. The value of $D_1$ tells about the disorder in a system. The correlation between neighbouring points is another important parameter in the investigation of fractal structures. From the whisker-and-box plot it is evident that the value of $D_1$ before and after exfoliation remain unaltered around $D_1 = 1.63$. It is interesting that the mean value of $D_0$, $D_1$, and $D_2$ before and after exfoliation remain the same as 1.72, 1.66, and 1.63 respectively. From this, it is evident that the fractality is preserved during the blooming of efﬂorescent carbon allotrope in the process of alkali-treatment and exfoliation.

4. Conclusions

Surface area enhancement has always been a fascinating area of research in nanoscience and nanotechnology. Morphological modifications developing brilliant patterns together with the larger effective surface area has become nano art today for diversified applications in nanoelectronics. In the present work, graphite, graphene, and soot containing carbon allotropes are subjected to morphological analysis before and after alkali-treatment.
and ULPE. The camphor, diesel, and petrol soot are found to develop brilliant flower-like structures from the spindle-like base units as a result of Ostwald ripening. When graphite forms bouquet-like structures, graphene shows teared petal-like structures upon exfoliation. The XRD analysis of graphite, graphene, and soot containing carbon allotropes unwraps the structural composition of the samples. The formation of various patterns through Ostwald ripening and agglomeration of CNPs is a complex process. The fractal analysis is one such technique that can be employed for complexity mapping. The analysis reveals a multifractal structure to the samples with the values of $D_0 (1.72)$, $D_1 (1.66)$, and $D_2 (1.63)$ preserved upon the blooming of efflorescent carbon allotrope during exfoliation. The study shows that ULPE not only enhances the effective surface area but also develop brilliant flower-like morphologies as if the carbon allotropes effloresce. Thus, the study suggests a method of turning futile soot for fruitful applications.

Conflict of interest
The authors declare no competing financial interest.

Data availability statement
All data that support the findings of this study are included within the article.

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