

# Nanoreactor-Enabled Formation of Graphitic Film from a Non-Graphitizing Precursor at Low-Temperature

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## Abstract

Graphite is produced by long term heating graphitizing precursors such as coke to 3000°C. However, most organic precursors are non-graphitizing which cannot develop graphite structure even at these super high temperatures. Gas-phase methods for graphite/graphene production, such as chemical vapor deposition (CVD), yield high-quality products but demand catalysts, substrates, high-purity hydrocarbon gases, specialized furnaces, and temperatures exceeding 1000 °C. Here, we demonstrate the synthesis of highly graphitized films with crystalline domains via low-temperature carbonization (900 °C) of nanoporous polydivinylbenzene (PDVB) microspheres, without the need for a CVD system or catalysts. The films formed on the inner surface of the furnace quartz tube and were characterized by Raman spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, X-ray Diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM). The Raman spectrum revealed a high graphitization degree ( $I_{D_1}/I_G = 0.78$ ), surpassing reported values for catalyst-free plasma- or low-pressure-assisted CVD. XRD showed a sharp diffraction peak at  $2\theta = 26.37^\circ$  ( $d = 3.37 \text{ \AA}$ ), exactly matching the diffraction peak of the (002) plane of Graphite-2H, while HRTEM and selected area electron diffraction confirmed crystalline domains with p63/mmc symmetry. We propose that the intricate network of nanopores as nanoreactors in PDVB microspheres enables the generation and controlled release of fused benzene rings into the quartz tube, where they condense to form crystalline films. This approach reveals how a nanoscale confinement can be translated into a macroscopic, scalable route, offering a low-cost and facile method for graphite or graphene production.

**Keywords:** Nanoreactor, Graphite, Non-Graphitizing, Catalyst-Free, Nanoconfinement

## 1. Introduction

Graphite, which is composed of stacked layers of graphene held together by  $\pi$ - $\pi$  interactions, enables high electron and ion conductivity. The  $sp^2$  hybridization of carbon atoms within the graphene layers also imparts high chemical and mechanical stability to this material. These properties, along with its low cost, have made graphite an unrivaled candidate for use as an anode in batteries and supercapacitors.<sup>[1],[2]</sup> The increasing demand for high-quality graphite in lithium batteries and supercapacitors which is used in applications ranging from electronics to electric vehicles, and the controllability of synthetic graphite properties, have prompted researchers to develop novel, cost-effective, and scalable graphite production methods.

Synthetic graphite is typically made by high-temperature heat treatment of organic precursors which involves heating to  $\sim 3000^\circ\text{C}$  for over 48 hours<sup>[3]</sup>, which is both energy-intensive and costly. However, the more challenging issue of graphitization is the seriously limited choice of graphitizable precursors. Only a small group of organic compounds can form crystalline graphite<sup>[3-6]</sup>, while most of them decompose into porous, disordered carbon<sup>[6]</sup>. Franklin<sup>[7]</sup> called the former graphitizing (Gr) precursors which include coal tar pitch, petroleum coke and the like, and the latter non-graphitizing (NGr) precursors involving synthetic or natural polymers like cellulose, chitin, polystyrene, and so on.

It is well known that synthesis from the gas phase typically leads to higher crystallinity compared to solid-state routes. Chemical vapor deposition (CVD) as a reliable gas phase method has been utilized to produce highly crystalline graphite in 1994<sup>[8]</sup>. However, following the discovery of graphene in 2001, this pathway was adopted to create few-layer or multilayer graphene<sup>[9]</sup>. The process involves charging a high-purity hydrocarbon gases, such as methane,

which is carried on a neutral gas mixed with pure hydrogen gas, to a CVD furnace tube consisting of different thermal zones equipped with a metal catalyst layer (copper or nickel) on a Si/SiO<sub>2</sub> substrate. At elevated temperatures above 1000°C, a thin layer of graphene is formed.

Although CVD leads to high quality graphene/graphite, but this method is associated with these challenges: i) complexity: the need for high-purity hydrocarbon and hydrogen gases, an accurate furnace with different thermal zones, procedure for removing catalyst layer and, transferring the graphene layer for the desired purpose, ii) impurity: from the dissolution of catalyst and substrate atoms in the produced layer, iii) high cost, and iv) limited size of final product: limited to the size of the substrate.

Recent research has focused on catalyst-free graphene synthesis to overcome part of the production challenges. Loung and colleagues<sup>[10]</sup> used joule heating of solid carbon precursors, achieving graphene with turbostratic stacking. Kotbi et al.<sup>[11]</sup> synthesized graphene from ethylene gas via low-pressure plasma and flash heating on various substrates, but none produced highly crystalline graphene with low I<sub>D</sub>/I<sub>G</sub> ratios. Papale and co-workers<sup>[12]</sup> applied plasma-enhanced CVD to orange oil on silicon and quartz substrates, without achieving high crystallinity. Liu's team<sup>[13]</sup> used single-crystal Si wafers and carbon monoxide gas as the carbon source, but the graphitic structures only formed at temperatures higher than 1000°C. To the best of our knowledge, there is no report on a scalable gas-phase synthesis of graphene/graphite without using a catalyst, a CVD furnace with different thermal zones, pure hydrogen gas, and a substrate at a low temperature.

Divinylbenzene (DVB), composed of one benzene ring (fundamental part of graphene/graphite structure) and two vinyl arms, polymerizes to form a thermoset polymer and if sulfonated in sulfuric acid, it yields 40% carbon material after carbonization to 1000°C<sup>[14]</sup>, which is a high yield amongst polymers. Also, increasing the surface area of this polymer is

easily achieved by employing aromatic and/or aliphatic hydrocarbons as porogens in the initial mixture <sup>[14]</sup>.

Despite its promise, PDVB has generally failed to produce graphitic carbon. Asfaw and co-workers studied the carbonization of sulfonated polystyrene-co-poly(divinylbenzene) polyHIPEs to 1500°C <sup>[15]</sup>, and no high degree of graphitization was obtained at such a high temperature. Even by employing iron as a strong catalyst, Liu and colleagues <sup>[14]</sup> could not develop graphite structure to a high extent. Similar results were recorded for PDVB, poly(PDVB-co-vinylimidazole)<sup>[16]</sup>, hyper crosslinked <sup>[17]</sup> or nitrogen-doped poly(St-DVB) <sup>[18]</sup> samples.

In our previous study <sup>[19]</sup>, we demonstrated that nanopores in an NGr precursor (sulfonated polydivinylbenzene (PDVB) microspheres) can act as dynamic nanoreactors, enabling the local fusion of benzene rings resulting from the decomposition of pore walls and conversion to fused benzene rings (FBRs) followed by graphitic structure development inside pores at low temperature. However, that work was limited to microscale particles, and the broader implications of considering nanoreactors network (the nanoporous intricate structure) function for forming extended graphitic architectures out of microspheres remained unexplored. Here, we apply the nanoreactor concept to demonstrate the growth of graphitic films directly on the walls of a quartz tube at the low temperature of 900 °C (compared to 3000 °C in graphitization and T>1000 °C in CVD production method), without catalyst, substrate, or CVD processing.

This approach reveals how a nanoscale confinement effect can be translated into a macroscopic, scalable route for graphitic film production. By bridging the gap between confined graphitization in microspheres and extended film growth, this work advances the importance of microstructure engineering for facilitating molecular self-assembly pathways instead of atomic carbon arrangement for graphite crystallization and provides a foundation for low-cost, scalable synthesis of graphitic materials.

## 2. Experimental Procedure

### 2.1. Ingredients

Divinylbenzene monomer (DVB),  $\alpha,\alpha'$ -azobisisobutyronitrile (AIBN) as an initiator, polyvinylpyrrolidone (PVP) as a stabilizer, hexadecyl trimethyl ammonium bromide (CTAB) as a surfactant, toluene and n-heptane as pore generating agents (porogens), and concentrated sulfuric acid (95-97%) were all purchased from Merck.

### 2.2. Synthesis of hierarchal porous carbon microspheres

Porous PDVB microspheres were synthesized using a microemulsion polymerization method. The aqueous phase was prepared by dissolving 3.75 mg of polyvinylpyrrolidone (PVP) and 1.65 mg of cetyltrimethylammonium bromide (CTAB) in 50 mL of deionized water. The oil phase consisted of 2.5 mL toluene, 1.25 mL n-heptane, 6 mg of azobisisobutyronitrile (AIBN) as the initiator, and 1 mL divinylbenzene (DVB) monomer. The aqueous and oil phases were emulsified at 12,000 rpm for 2 min using a Heidolph Silent Crusher homogenizer. Polymerization was then conducted in a three-neck flask under an argon atmosphere at 65°C for 6 hours. After completion, the reaction mixture was rapidly cooled to room temperature.

The polymer microspheres were collected by centrifugation at 9,000 rpm for 20 min. The precipitated microspheres were washed with a 50:50 (v/v) mixture of deionized water and ethanol to remove impurities. Finally, the washed white pellet was dried in a petri dish at 80°C for 24 hours in a Memmert dryer and labelled as PDVB.

### 2.3. Sulfonation

A two-neck Pyrex balloon equipped with a condenser was charged with 35 mL of concentrated sulfuric acid and heated to 80°C. Subsequently, 0.8 g of PDVB powder was added to the acid, forming a suspension that was stirred continuously at 100°C for 12 hours. During this period, the suspension's color changed from red to dark brown, indicating the progress of

sulfonation. After 12 hours, the suspension was separated using a ceramic membrane filtration. The solid sulfonated PDVB was washed repeatedly with an excess amount of distilled water until the pH of the washing filtrate reached neutral (pH 7). Finally, the sulfonated PDVB was dried at 80°C for 24 hours in a Memmert oven.

#### **2.4. Carbon coating formation via Carbonization**

Sulfonated porous PDVB microspheres were carbonized to 900 °C for 2 h with the heating rate of 2.5 °C/min in a tubular furnace equipped with a quartz tube under a continuous argon gas flow. The quartz tube used had a length of 1.5 m and an inner diameter of 2 cm. The furnace's hot zone spanned 20 cm in the center of the tube. The quartz tube was not cleaned between consecutive carbonization runs. Instead, a new PDVB sample was charged in the furnace, following the same heating profile to promote the deposition and reaction of decomposition products inside the tube. Over multiple cycles, a carbonaceous coating with a greyish luster accumulated on the interior walls of the quartz tube.

#### **2.5. Characterization**

This deposited matrix was carefully separated from the tube and designated as GCNP (stands for graphitized coating from NGr polymer). The GCNP material was characterized using scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM).

SEM was conducted using a VEGA TESCAN scanning electron microscope at 20 KV. Prior to the analysis, the separated coatings from the quartz tube were sonicated in ethanol for 10 min. Fourier-transform infrared (FTIR) spectroscopy was performed using a PerkinElmer spectrometer with 2 cm<sup>-1</sup> resolutions in 400-4000 cm<sup>-1</sup>. The Raman spectrum was recorded by a Raman spectrometer employing an Nd:YAG laser at 532 nm with the power of

90 mW. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer, using Cu K $\alpha$  radiation with 0.04° resolution.

The graphitization degree was calculated by the Mering and Maire equation and crystallite size was obtained by the Scherrer equation [20]:

Degree of graphitization from Mering and Maire equation:

$$g = (0.3440 - d_{002}) / (0.3440 - 0.3354) \quad (1)$$

Crystallite size:

$$\text{lateral crystallite size, } L_a = (k_1 \lambda) / [\beta(100) \cos \theta(100)] \quad (2)$$

$$\text{vertical crystallite size, } L_c = (k_2 \lambda) / [\beta(002) \cos \theta(002)] \quad (3)$$

Here,  $\beta$  is the peak half-height width, and  $k_1$  and  $k_2$  are 1.84 and 0.89, respectively.

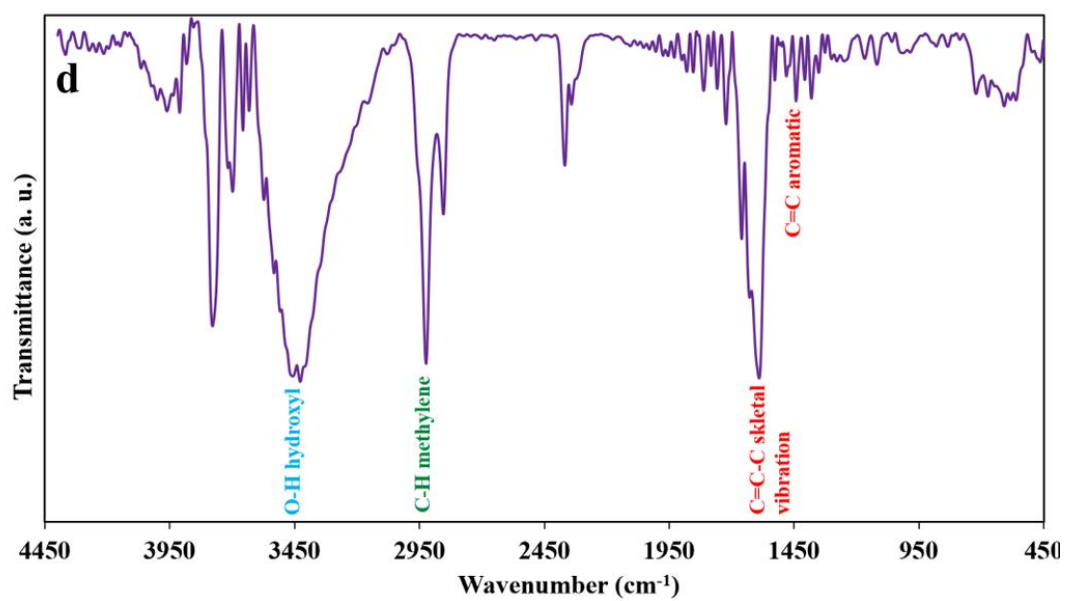
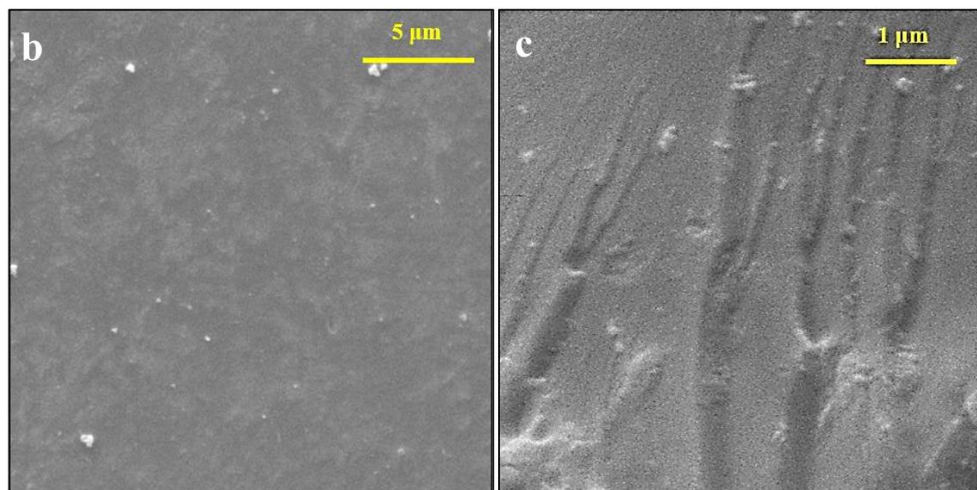
High-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were recorded on an FEI Tecnai G2 20F SuperTwin transmission electron microscope at 200 kV. Prior to imaging, samples were dispersed in ethanol by sonication and dropped onto copper grids. HRTEM data analysis was carried out using the digital micrograph software (version 3.40.2804.0).

### 3. Result and Discussion

The created carbon coating on the interior wall of the quartz tube as a result of repeatedly low-temperature carbonization of sulfonated PDVB (GCNP) was precisely separated from the tube and was characterized structurally and chemically without further processing.

#### 3.1. Structural and chemical analysis of the sample

Figure 1 shows images of the GCNP sample along with its Raman and FTIR spectra.



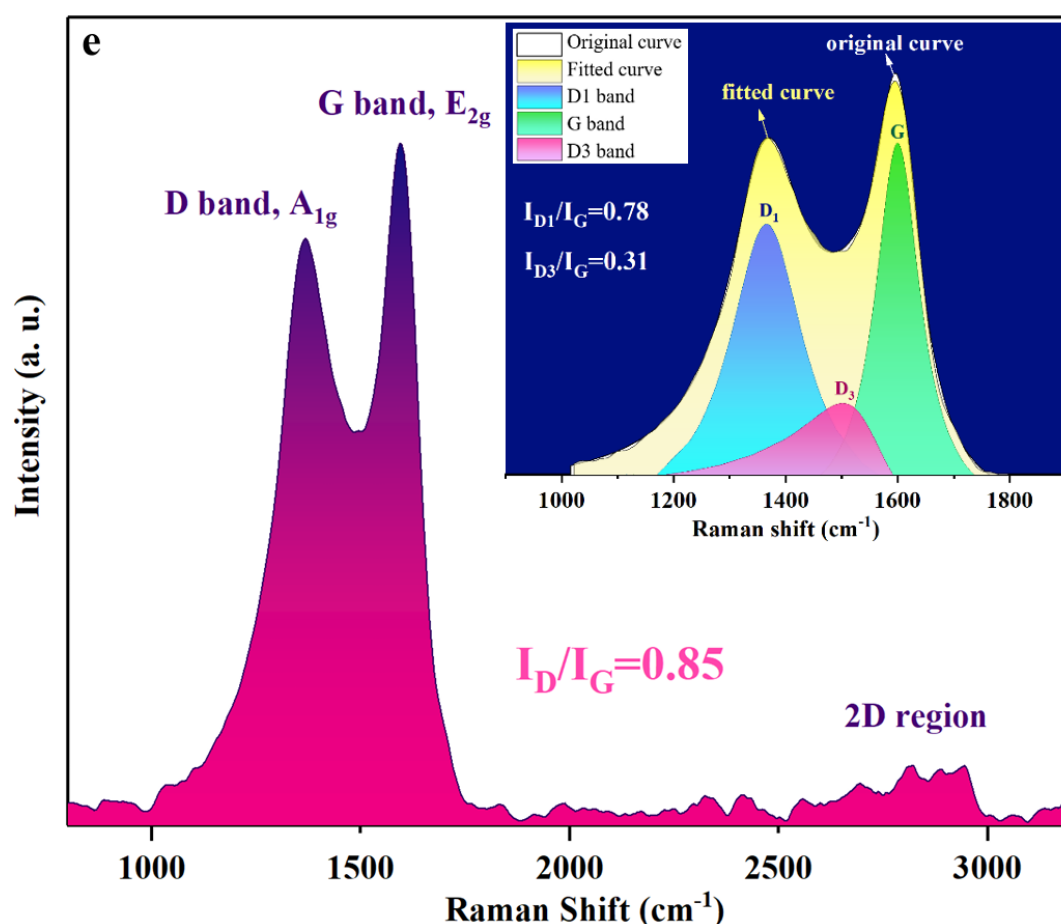


Figure 1. a) The quartz tube of the tubular furnace in which several low-temperature carbonization of NGr polydivinylbenzene microspheres was conducted. Left: The grayish lustrous coating in a solid state formed along the tube. Right: the carbonaceous matrix separated from the tube and labeled as GCNP. b) SEM image of the coating, showing the uniformity of it. c) side view of the sample indicating the layer by layer growth of the coating d) FTIR spectrum of GCNP sample showing the existence of high amount of fused benzene rings as well as aliphatic chains. e) Raman spectrum of GCNP showing the higher G to D intensity ratio ( $I_D/I_G=0.87$ ), indicating the high graphitization degree of the sample the inset shows the deconvolution of Raman peaks to precisely indicate the share of crystalline to amorphous part in the sample.

In Fig1a (left), the quartz tube with a lustrous gray color coating is seen in which nanoporous sulfonated PDVB microspheres were carbonized to 900°C. The coating was easily separated from the tube. In the right photo, the collected sample is shown. Figures 1b and c show SEM images of the GCNP sample. From Fig.1b it can be seen that the synthesis process has led to the formation of a crack-less and almost uniform coating. In Fig.1c, the layer-by-

layer formation of the film from the carbonization of nanoporous sulfonated PDVB microspheres is observed. To evaluate the graphitization level of this matrix, it was characterized by Raman and FTIR analysis.

The FTIR spectrum of the GCNP sample is shown in Fig.1d. The vibration bands in 1380  $\text{cm}^{-1}$  are related to the symmetric deformation vibration of methyl (umbrella mode), while 1408, 1442 and 1480  $\text{cm}^{-1}$  originate from the stretching vibrations of the C=C aromatic bond (ring mode) [21]. The intense absorption band in 1590  $\text{cm}^{-1}$  with shoulders in 1628 and 1660  $\text{cm}^{-1}$  arises from the C=C-C skeletal vibration in 6-membered carbon rings with  $\text{sp}^2$  hybridization [21],[22]. On the other hand, 2854 and 2924  $\text{cm}^{-1}$  are assigned to the symmetric and asymmetric stretching vibrations in methylene chains, respectively [22-24]. Hydroxyl groups due to the water adsorption are identified by the 3424  $\text{cm}^{-1}$  vibrational mode as well [25].

Upon heat treatment of sulfonated PDVB during carbonization, due to the bond breaking, benzene ring free radicals besides small aliphatic chains are released [19]. Our previous study confirmed the presence of an intricate and hierarchical porous structure in PDVB microspheres consisting of small ink-bottle mesopores and ultramicropores [19]. These pores lead to the local increased pressure due to the confinement of decomposition products inside pores nanoscale spaces. This condition results in the action of nanopores as nanoreactors to convert benzene free radicals to FBRs. The existence of C=C-C skeletal vibration sharp band implies that despite the complex pore structure of microspheres that makes the exit egress of nanoreactors products difficult, part of FBRs succeed in escaping to the furnace free space and arrive at the carbon coating deposit onto the forming carbon coating.

The Raman spectrum of the sample (Fig.1e) exhibits two G and D bands in — at approximately 1597  $\text{cm}^{-1}$  and 1366  $\text{cm}^{-1}$ , respectively. The former is assigned to the  $\text{E}_{2g}$  symmetry related to the  $\text{sp}^2$  hybrid in carbon materials. This vibration mode directly reflects the in-plane ordered arrangement of fused 6-membered carbon atoms with a hexagonal shape.

On the other hand, the latter, i.e. the D-band arises from the  $A_{1g}$  symmetry, the breathing mode of the carbon ring. This mode can only activate ~~on~~ at the edges of graphene layers or defective carbon rings [25-27]. However, this two-peak pattern generally consists of more peaks.

The more ~~the~~ ordered the arrangement of carbon rings and crystallite length of graphene layers, the less the intensity of the D to G band ratio. Also, the position of the G-band can determine the stacking of graphene layers. If the number of stacked layers increases, the G-position shifts to lower frequencies [29], [30]. Therefore, the  $I_D/I_G$  ratio as well as the G-position should be considered to evaluate the graphitization degree of the material. According to this criterion which was addressed by Ferrari and Robertson [30] (G-position=1597.917  $\text{cm}^{-1}$ ,  $I_D/I_G=0.85$ ) GCNP is in the Graphite region and is predicted to ~~have low~~ consist of few stacked graphene layers. Compared to our previous study in which the carbonized sample showed ~~the  $I_D/I_G=0.87$~~  an  $I_D/I_G$  ratio of 0.87 and G-position of 1587.591  $\text{cm}^{-1}$  [19], it is expected that the GCNP sample shows a higher graphitization degree consisting of larger crystallite length and fewer graphene layers in average.

To assess the graphitization degree in more detail, the spectrum was deconvoluted and ~~was~~ found to consist of three peaks at approximately 1365, 1500, and 1599  $\text{cm}^{-1}$ , corresponding to the  $D_1$ ,  $D_3$ , and G bands, respectively (inset in Fig.1d). The  $D_1$  band is attributed to carbon atoms near the edges of graphene layers [27], while the  $D_3$  band originates from the amorphous carbon fraction in the material [27], [31], [32]. From the deconvoluted curve, the  $I_{D_1}/I_G$  and  $I_{D_3}/I_G$  ratios were determined to be 0.78 and 0.31, respectively, indicating that the production pathway favors the synthesis of a low-amorphous, highly crystalline product. However, the in-plane growth of the graphene layers remains limited.

In the absence of ~~any similar studies to the present work~~ directly comparable studies, to the best of our knowledge, ~~a review of catalyst-free CVD investigations however rare~~ we

compare our results with the rare reports of catalyst-free CVD, ~~was conducted~~ to evaluate the graphitization degree achieved in this work. Kotbi and co-workers <sup>[11]</sup> synthesized graphene from ethylene gas by low-pressure plasma followed by flash heating. Substrates included silicon, quartz, tin oxide, glass and polyamide. In none of these cases, a highly crystalline graphene with an  $I_D/I_G$  ratio of less than 1 was reported. Papale et al. <sup>[12]</sup> used orange oil gas as a carbon source and conducted a low-pressure plasma-enhanced CVD on a silicon wafer or a quartz substrate. This study also failed to produce graphene layers with an  $I_D/I_G$  ratio even close to 1. These comparisons highlight the exceptional nature of achieving such a low intensity ratio in our work.

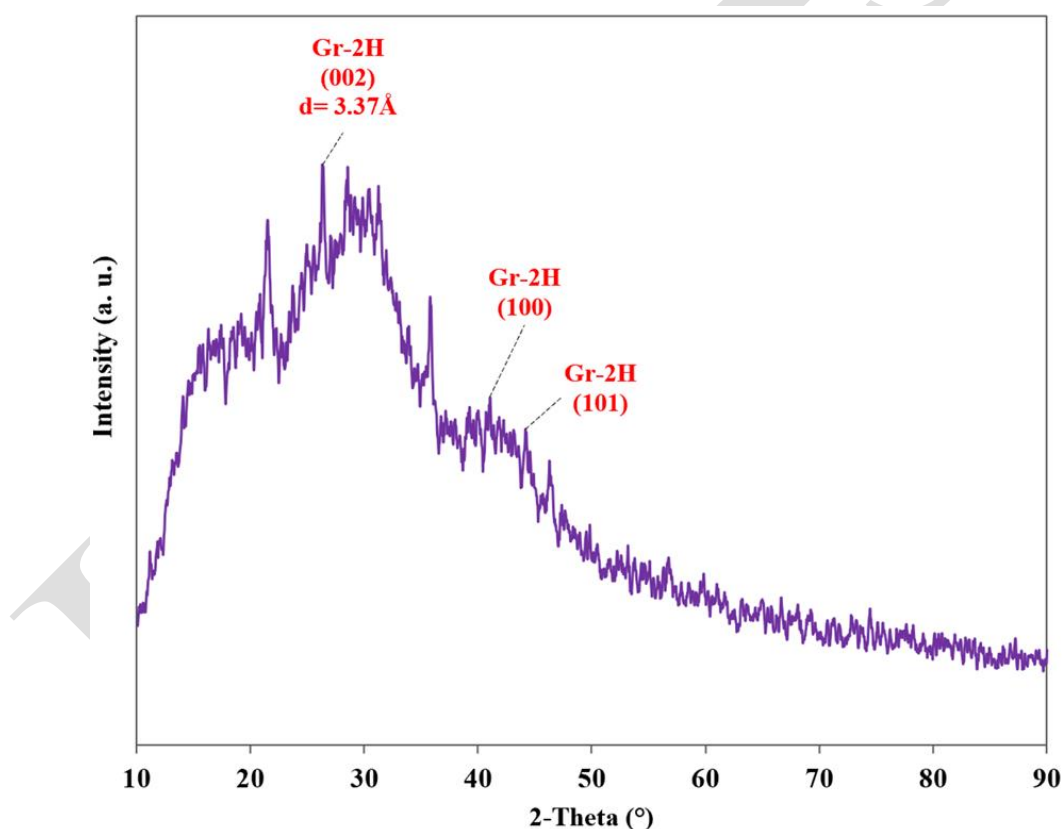


Figure 2. XRD pattern of GCNP sample ~~representing~~ indicating the composite nature of the material consisting of crystalline and amorphous phases. The inset shows the comparison of the sample peaks with Graphite-2H (PDF 41-1487) which matches to a high extent.

Table 1. Comparison between GCNP sample and Graphite-2H (PDF 41-1487) diffraction peaks

| GCNP      |         | Graphite-2H (PDF 41-1487) |         | (hkl) |
|-----------|---------|---------------------------|---------|-------|
| $2\theta$ | d(Å)    | $2\theta$                 | d(Å)    |       |
| 26.37375  | 3.37661 | 26.382                    | 3.37557 | 002   |
| 41.0775   | 2.19558 | 42.223                    | 2.13863 | 100   |
| 44.22505  | 2.04634 | 44.393                    | 2.03901 | 101   |

The XRD pattern of the GCNP sample (**Fig.2**) shows a broad peak along with superimposed sharp peaks, exhibiting its composite nature. This pattern is similar to that of the CAR-900 sample in our previous study <sup>[19]</sup>, while the presence of sharp peaks in  $2\theta=26.37^\circ$ ,  $41.07^\circ$  and  $44.25^\circ$  distinguishes it from that. These peaks are related to the d-spacings of 0.337, 2.195 and 2.046 nm, assigned to the ~~crystalline~~ crystallographic planes of (002), (100) and (101) in Graphite-2H (JCPDF card-411487, **Table 1**), respectively. The interlayer d-spacing of Graphite-2H from (002) crystalline planes in the PDF card is 0.337 nm which exactly matches that of the present sample.

The degree of graphitization was also calculated from Maring and Marie equation [20] (equation (1)) and found to be 74% which is a high value for a catalyst/substrate-free carbonization at 900°C. For most carbons prepared at low temperatures, whether or not using catalysts, a two-broad peak pattern is reported, implying an amorphous structure formation in the material <sup>[33-35]</sup>. The highly crystalline nature of GCNP obtained from XRD analysis is in agreement with Raman results.

The crystallite thickness along the c-axis ( $L_c$ ) and the basal plane crystallite size along the a-axis ( $L_a$ ) were calculated by the Scherrer equation from the (002) and (100) peaks, respectively (equations (2) and (3)). ~~The relative value for  $L_c$  was obtained as~~ The  $L_c$  value was calculated to be ~23 nm, which shows ~69 graphene layers stacked in average for this sample, while  $L_a$  was calculated to be ~68 nm. The observed discrepancy between the high in-

plane crystallite size and relatively moderate stacking order indicates that the process conditions are more conducive to lateral graphene sheet formation than to the alignment of these sheets into stacks. This result proved Raman result about the formation of graphitic structure with graphene layers of limited in-plane crystallite size.

It should be noted that, due to the low temperature applied during carbonization (900°C), some ~~organics are still available~~ organic residues are still present (FTIR spectrum, aliphatic groups in 1380, 2854 and 2924  $\text{cm}^{-1}$ ), which is responsible for the appearance of other sharp peaks in  $21.51^\circ$  and  $35.82^\circ$ , since these peaks are available in JCPDS cards 31-1705, 40-1995, 50-2246, 4-0365, 40-1892, and the like. The appearance of these peaks was also reported by other researchers as well [36-38].

### 3.2. HRTEM study of the sample

To study the GCNP sample in more detail, HRTEM analysis was used to identify the studied sample microstructure. SAED patterns were recorded and FFT images were calculated to determine the crystallographic characteristics of the investigated region as well. HRTEM micrographs and calculated SAED patterns are depicted in **Fig.3**.

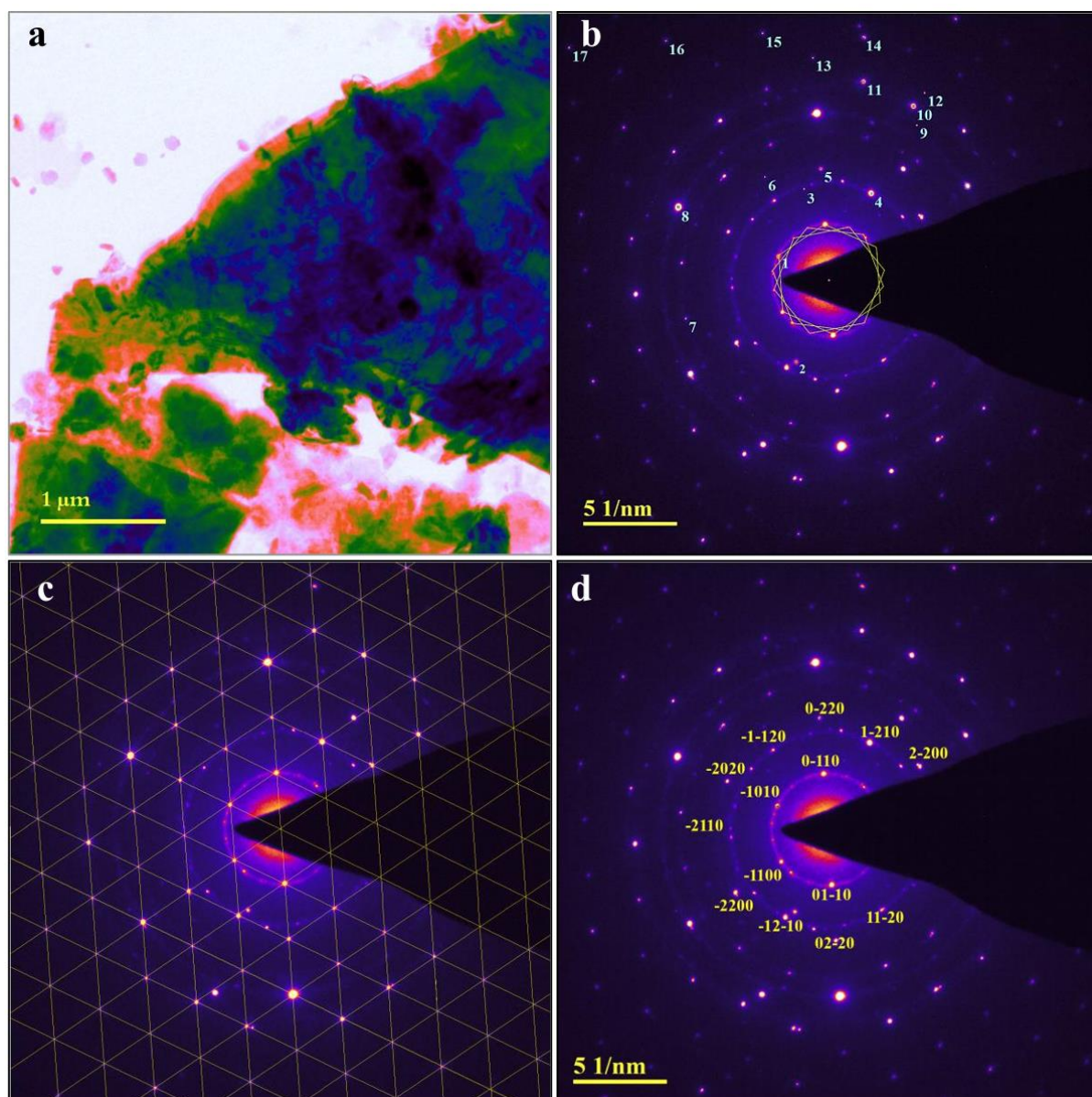


Figure 3. a) TEM image of GCNP consisting of large multilayer particles besides small hexagonal flakes (upper left of the image, restricted in a small rectangular). b) SAED pattern of the TEM image(a), composed of a significant number of diffraction spots covering all the entire pattern and a few narrow circles. This pattern is attributed to the existence indicates the presence of crystalline areas with large sizes as well as polycrystalline areas. The hexagonal arrangement of spots shows a  $p6mm$  symmetry of the crystals. The related crystalline planes according to d-spacings calculated from the radius of spots are presented in Table 2. Three hexagons in the central part of the pattern show the presence of at least three crystalline layers in the studied region. c) The SAED pattern meshed by parallel lines with a  $60^\circ$  angle passing through the spots of the pattern, showing the exceptionally highly ordered structure of the sample. d) The indexed SAED pattern obtained from solving the hexagonal crystal lattice.

Fig.3a shows a region containing several layers and small hexagonal flakes formed beside it. Surprisingly, in the SAED pattern of this image (Fig.3(b)), a significant number of diffraction spots in a hexagonal arrangement which have filled all over the pattern, as well as a few narrow rings are seen. The appearance of too many spots covering all the entire pattern in a hexagonal shape implies that there are highly crystalline domains of large sizes compared to larger than the coherence width of the electron beam. To highlight the exceptionally highly ordered arrangement of the spots in Fig.3(b), parallel lines with a 60° rotation angle and constant distances were drawn which result is displayed in Fig.3 c. These lines have passed through all spots. Such a full spot diffraction pattern representative of a super high crystallinity has been reported for multilayer graphene <sup>[38]</sup> or natural graphite so far <sup>[39]</sup>. In Fig.3d, the identified crystalline planes as a result of solving the hexagonal lattice are presented.

Table 2. Calculated d-spacings in Fig.3(b) and comparison with Graphite-2H PDF card 41-1487 which resulted in the determination of related crystalline planes. Different green shades represent the difference between the d-spacings of Graphite-2H and the GCNP sample. Dark greens stand for the closest amounts to those of the reference card, while light green is attributed to the larger difference between them. Spots 11 to 17 are related to the higher-order reflections of the main d-spacings second, third and fourth order of main d-spacings in the reference card.

| Spot | GCNP<br>d-spacing (Å) | Graphite-2H<br>PDF 41-1487 d-spacing (Å) | $\Delta d = d_{\text{Graphite-2H}} - d_{\text{GCNP}}$ (Å) | (hkl)  |
|------|-----------------------|------------------------------------------|-----------------------------------------------------------|--------|
| 1    | 3.376                 | 3.37563                                  | 0.000370                                                  | (002)  |
| 2    | 2.134                 | 2.13865                                  | -0.004650                                                 | (100)  |
| 3    | 1.993                 | 2.03901                                  | -0.046010                                                 | (101)  |
| 4    | 1.956                 | 2.03901                                  | -0.083010                                                 | (101)  |
| 5    | 1.68                  | 1.6811                                   | -0.001100                                                 | (004)  |
| 6    | 1.55                  | 1.54777                                  | 0.002230                                                  | (103)  |
| 7    | 1.269                 | 1.23408                                  | 0.034920                                                  | (110)  |
| 8    | 1.125                 | 1.12084                                  | 0.004160                                                  | (006)  |
| 9    | 1.057                 | 1.05672                                  | 0.000280                                                  | (201)  |
| 10   | 0.9735                | 0.9924                                   | -0.018900                                                 | (114)* |
| 11   | 0.9343                | 0.903685                                 | 0.030615                                                  | (204)  |
| 12   | 0.8947                | 0.903685                                 | -0.008985                                                 | (204)  |
| 13   | 0.8434                | 0.8439075                                | -0.000508                                                 | (008)  |
| 14   | 0.767                 | 0.773885                                 | -0.006885                                                 | (206)  |
| 15   | 0.7367                | 0.71288333                               | 0.023817                                                  | (300)  |
| 16   | 0.65                  | 0.67967                                  | -0.029670                                                 | (303)  |

\*This peak is not available in PDF card 41-1487. It was introduced in ref <sup>[40]</sup>.

D-spacings of spots were calculated and displayed in **Table 2**. Results showed that spots and rings belong to the Graphite-2H (JCPDS card 41-1487) structure which consists of graphene layers with ABAB stacking order. Based on the comparison with the JCPDS card 41-1487 one can find that only one crystalline plane (102) is absent in the SAED pattern of the sample which shows an absolutely highly crystalline nature of the studied area. In addition, this feature has led to the appearance of second, third and even fourth order of crystalline planes (spots 11 to 17 in Fig.3(b) and in Table 2).

After all, the lattice constants of the hexagonal unit cell of the sample which are calculated from (002) and (100) crystalline planes, as well as the comparison with Graphite-2H are listed in **Table 3**.

Table 3. Calculated lattice constants for GCNP studied area calculated from data in Table 2.

| plane | GCNP<br>d-spacing (nm) | Graphite-2H<br>(PDF 41-1487)<br>"a" lattice<br>constant (pm) | Graphite-2H<br>(PDF 41-1487)<br>"c" lattice<br>constant (pm) | GCNP<br>"a" lattice<br>constant (pm) | GCNP<br>"c" lattice<br>constant (pm) |
|-------|------------------------|--------------------------------------------------------------|--------------------------------------------------------------|--------------------------------------|--------------------------------------|
| (002) | 0.3376                 | -                                                            | 675.2                                                        | -                                    | 675.2                                |
| (100) | 0.2252                 | 246.9                                                        | -                                                            | 246.4                                | -                                    |

The "a" and "c" lattice constants which are the hexagonal unit cell dimensions ~~are obtained~~ were calculated to be 246.4 and 675.2 pm, respectively. In a hexagonal lattice, c is the distance between two A-A layers. On the other hand, a is the distance between two parallel sides of carbon hexagons. These parameters are schematically presented in Fig.4a and (b). From Table 3, it is concluded that these parameters are the same as the Graphite-2H unit cell. These data in accordance with data in Table 2 show that the studied region of GCNP in Fig.3

has crystallized to Graphite-2H structure to a superb high extent. The constructed structure according to the lattice parameters obtained in Table 3 is shown in **Fig.4**.

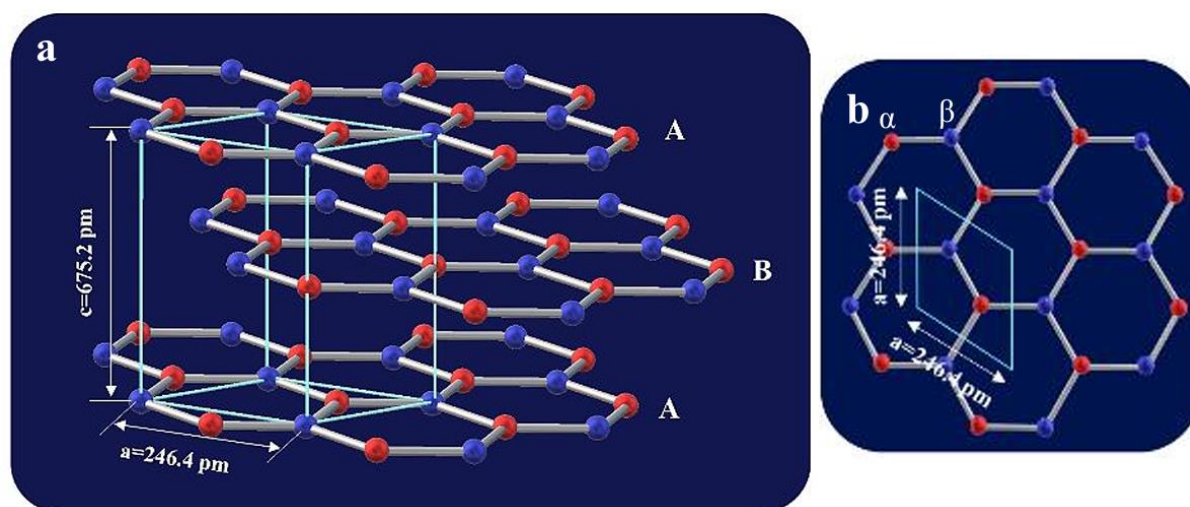


Figure 4. Constructed structure of graphite-2H according to the calculated lattice constants from SAED pattern a) Side view of the graphite structure with Bernal stacking order ABA. Red and blue spheres represent C atoms in  $\alpha$  and  $\beta$  positions sites of the Graphite basal plane (graphene layer). The corresponding unit cell is determined by a light blue rhombohedral prism. Dimensions of the prism are designed according to the lattice constants obtained from calculations of the SAED pattern, presented in Table 3. b) Top view of Graphite basal plane (a single graphene layer) in which the unit cell is displayed with a light blue rhombic shape. The lattice constant equals the calculated “a” shown in Table 3. The unit cell constants are in excellent agreement with the Graphite-2H unit cell (a lattice constant of Graphite-2H=0.246.9 pm and the c parameter of this structure is 675.2 pm).

In the following, the results of the HRTEM study of one of the hexagonal flakes in Fig.3a are presented.

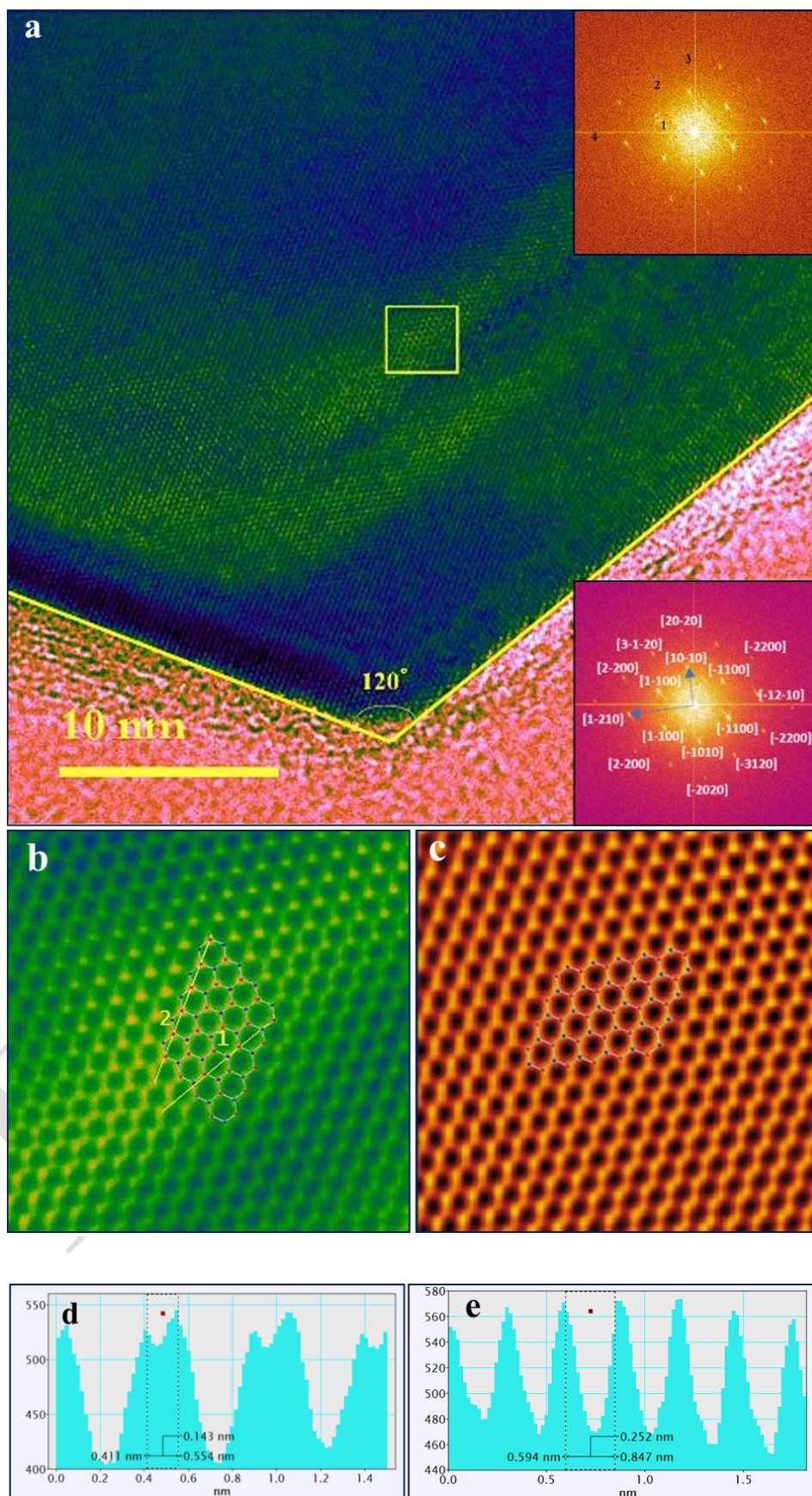


Figure 5. a) HRTEM image of one of the hexagonal flakes shown in the black rectangular in Fig.3a showing the high long-range order of 6-fold rings. The upper right inset shows the FFT pattern of the image consisting of large bright spots implying the very highly ordered arrangement of the studied region, resembling CVD-derived multilayer graphene. Respective dimensions of spots are calculated and listed in Table 4. The bottom right inset shows the indexed FFT pattern of the image. b) The enlarged area of yellow rectangular in the image(a), displays the perfect graphene sheet structure with p6mm symmetry on top of the flake, resembling an HOPG material. The designed honeycomb structure of the graphene sheet is seen in the image wherein red and blue circles are C-atoms occupied  $\alpha$  and  $\beta$  positions (Fig.4). c) The simulated IFFT image of the studied region in image(b) is formed by masking spots in the FFT pattern (inset of image(a)), illustrating the excellent hexagonal symmetry of the honeycomb structure in the graphene layer. d) and e) linear profiles of lines 1 and 2 showing the "a" lattice constant of the graphene sheet and C-C distance in 6-membered carbon rings in the graphene layer, respectively. These results show that the studied flake is one of the highly crystalline domains that has participated in the appearance of spots in the SAED pattern.

Table 4. Dimensions of spots marked on the FFT pattern (Fig.5b), show excellent compatibility with that of the graphene layer [41], [42] (Fig.4b).

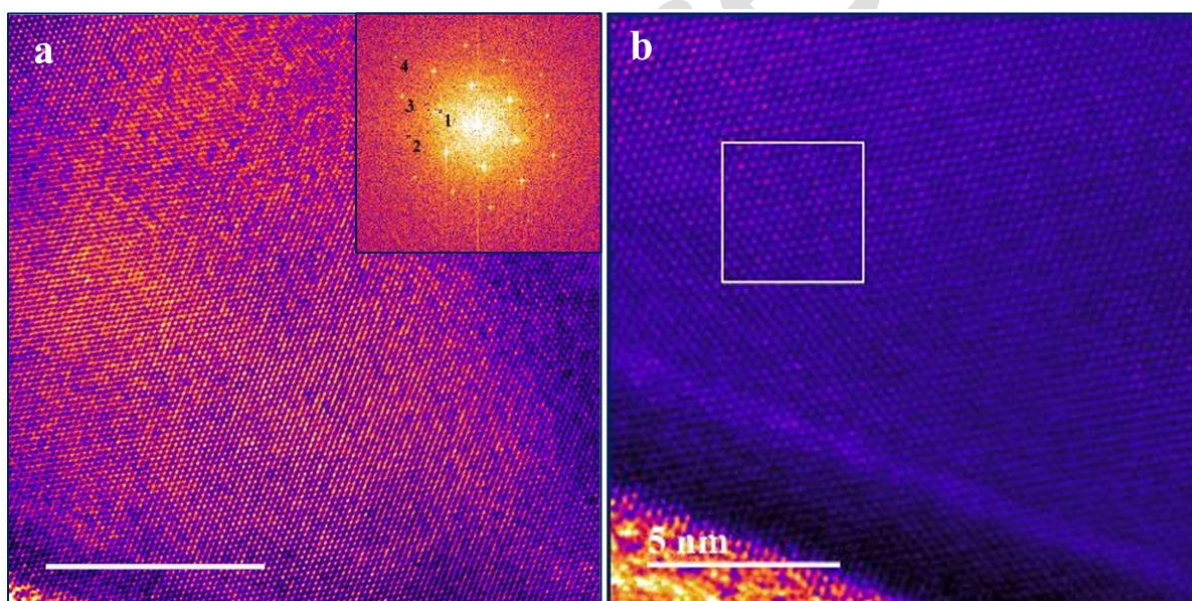
| Spot | dimension (nm) | attributed parameter according to graphene layer dimensions |
|------|----------------|-------------------------------------------------------------|
| 1    | 0.252          | "a" lattice constant                                        |
| 2    | 0.1454         | C-C length in 6-fold carbon ring                            |
| 3    | 0.1255         | "a/2"                                                       |
| 4    | 0.09543        | "3a/8"                                                      |

**Fig.5a** shows the HRTEM micrograph recorded from hexagonal flakes in Fig.3a. The highly crystalline particle with a  $120^\circ$  angle as well as a long-range order of small hexagons are seen. Further analysis via Fast Fourier Transform (FFT) is presented in the upper right inset of Fig.5a, showing bright spots indicative of the high symmetry of the structure. The related spot dimensions were calculated and are listed in **Table 4**. Also, the indexed pattern is seen in the bottom right inset.

Considering the graphene lattice and 6-fold carbon rings of the layer one can conclude that the carbon atoms in the studied region are crystallized to a graphene sheet to a very high

extent. The restricted area of the sample in Fig.5a which is illustrated with a yellow rectangular was enlarged to study the arrangement of carbon atoms in more detail (Fig.5b). From this image, carbon hexagons with a honeycomb structure are obviously seen. Also, the inverse FFT image was established which is shown in Fig.5c. These images clearly show the  $p6mm$  symmetry of carbon atoms in a graphene layer which resembles multilayer graphene resulted from CVD process <sup>[43], [44]</sup>. Remarkably, the dimensions of hexagons that appeared in the micrograph and inverse FFT image are equal to those of hexagons in a graphene sheet Fig.5b and (c)) <sup>[44], [45]</sup>.

To reveal the high crystallinity of the flake, the edge zone was further analyzed in higher magnifications.



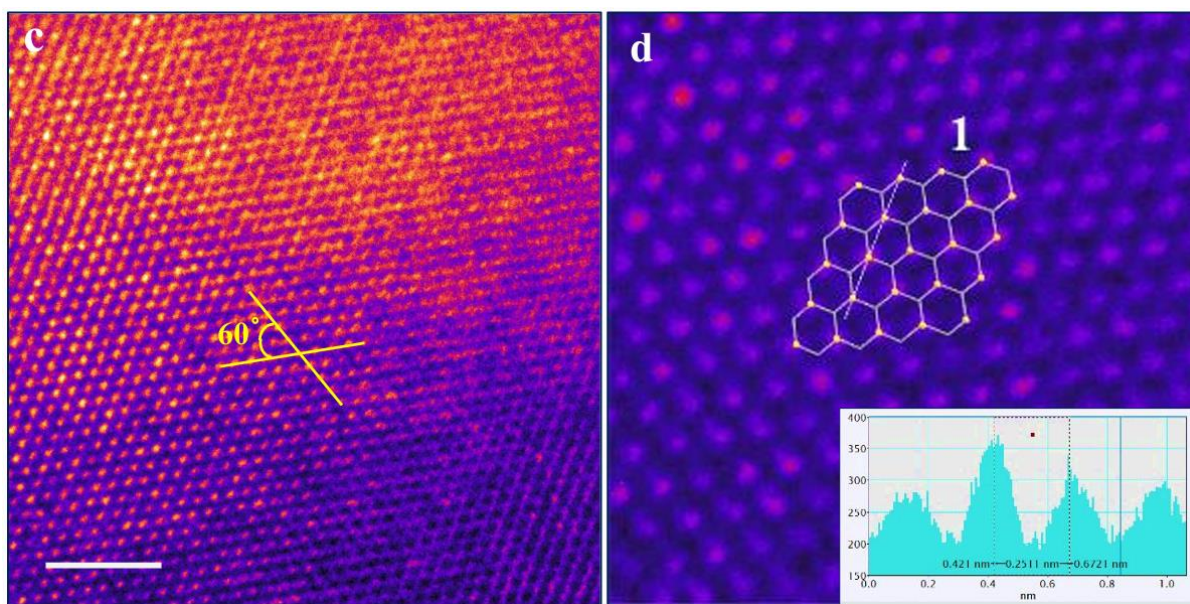
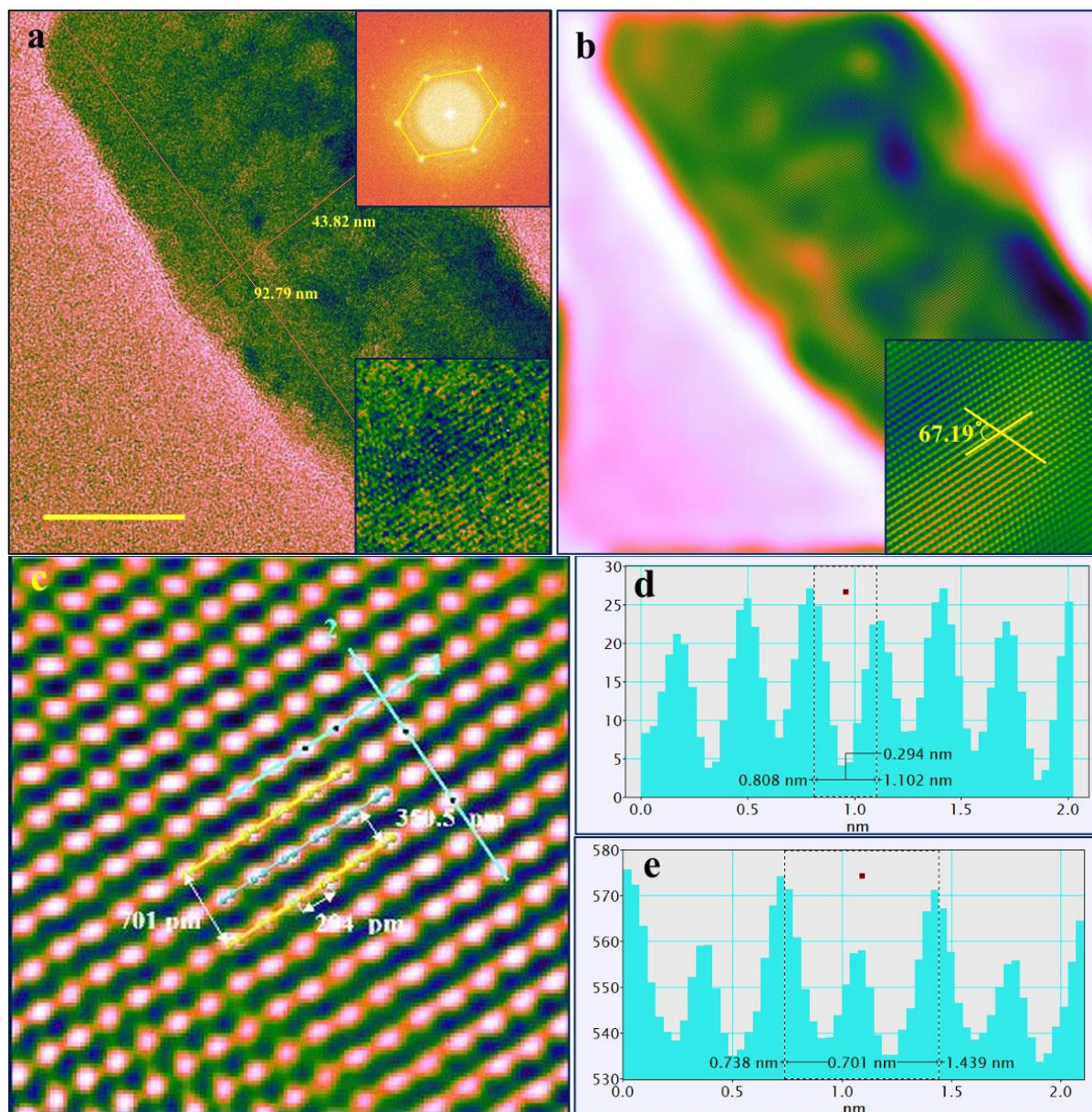


Figure 6. a) HRTEM image of the edge of crystalline flakes in Fig.5 showing a corrugation pattern of atoms arrangement. The inset displays the FFT pattern of the region including 20 bright spots like stars which show the hexagonal symmetry of the image(a). Parameters were equal to Table 4. b) and c) The edge of the flake with atomic resolution, revealing carbon atoms perfectly arranged in parallel lines with a  $60^\circ$  rotation angle. d) The enlarged area of white rectangular in the image(a) shows C-atoms (white points) with triangular arrangement instead of hexagons. These atoms are those carbon atoms that occupied the  $\beta$ -positions displayed in Fig.4b. Inset is the linear profile of line 1, indicating that C-atoms have 0.251 nm distance which is in agreement with “a” lattice of a graphene layer (Fig.4b).

HRTEM micrographs in **Fig.6** indicate the unambiguously highly crystalline nature of the flakes with higher resolution. To explore the symmetry of the region, an FFT image of Fig.6a was obtained which is illustrated in the inset. The parameters are the same as Table 4 which is quite equal to the graphene lattice. Micrographs of the studied area in higher resolutions are exhibited in Fig.6b, c and d wherein carbon atoms with a triangular arrangement are clearly seen. In analogy to graphene and graphite samples in which only  $\beta$ -atoms are visible [42], [46], in the present studied region only 3 atoms from 6 atoms in a 6-fold ring is seen. It is worth noting that in Bernal stacking ordered graphite (ABA sequence), the distance of  $\alpha$ -atoms (Fig.4b) from each other in AA layers equals the doubled amount of  $\beta$ -atoms due to the sliding of the B layer with respect to A layer. This affects the  $\pi$ - $\pi$  interaction between layers which

results in the disappearance of  $\alpha$ -atoms in some micrographs. In Fig.6d, the respective honeycomb structure with only  $\beta$ -atoms is displayed. Also, the line 1 profile of the micrograph was measured which showed the 0.251 nm distance between atoms. This length is equal to “a” lattice constant of graphene sheets [44].



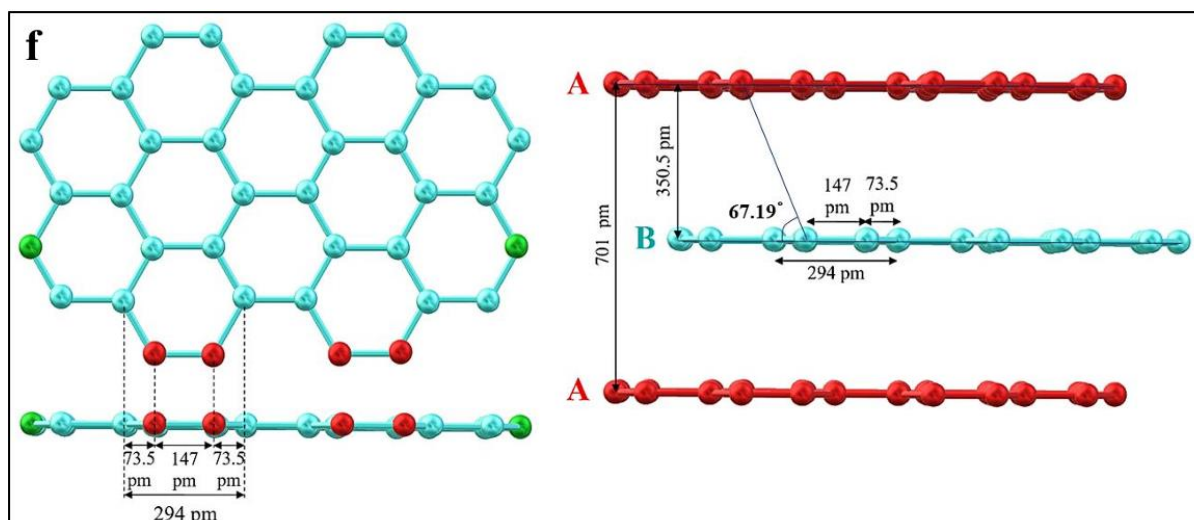


Figure 7. (a) HRTEM micrograph of a particle in the studied region of Fig.3a. The bottom right inset is the enlarged image of the particle in which lattice fringes are clearly seen. The FFT pattern (the upper left inset) shows large spots which indicate the existence of a highly crystalline zone. However, the stretched hexagon implies the presence of an anisotropic symmetry in the sample. b) The reconstructed inverse FFT image of the HRTEM micrograph was obtained by masking the spots of the FFT pattern to explore the crystalline nature of the sample without disorder. A layered structure comprising stretched points in every layer is observed very clearly. The inset shows the enlarged area of the IFFT image with an alternating layered structure. Also, the lines passing through the points show a  $67.19^\circ$  angle, the characteristic angle of lines passing through C-atoms in two AB layers (Bernal stacking order). c) The area with further zoom compared to the inset of (b) with the intra-layer point-to-point distance of 0.294 nm and inter-alternate layer d-spacing of 0.701 nm obtained from line profiles (d) and (e), respectively. These parameters are highly compatible with those of Graphite-2H if the side view is exposed to the electron beam (Fig.4a). Considering three layers in the image, every point is moved forward for one point-to-point distance in the middle layer, while the first and third layers are repeated alternatively so that points are exactly along each other. These features confirm the existence of Bernal stacking order in the sample. The schematic on the image shows the ABA stacking of graphene layers in the Graphite-2H structure which is in accordance with the IFFT image of the sample to a high extent. f) The schematic illustration of Bernal stacking order in Graphite-2H with dimension according to what is measured in (d) and (e) line profiles. This particle is another completely crystalline graphite in the sample.

**Fig.7a** shows the HRTEM micrograph of another particle in the GCNP sample. The zoomed area of the sample is displayed in the bottom right inset of Fig.7a for which lattice

fringes are obviously observed. No grain boundary or change in growth direction was seen for this large particle which is close to 1  $\mu\text{m}$  in length, implying the existence of a completely crystalline domain. The FFT pattern of this particle was produced (the upper left inset of Fig.7a). The appearance of an ordered hexagonal arrangement of spots indicates the existence of a highly ordered hexagonal structure of the sample. However, the distance between spots in the central hexagon varies by moving from one spot to another.

This stretched hexagon in addition to the presence of other 10 spots in only two quarters of the image, indicates that the crystalline structure of the particle has an anisotropic character. To study the crystalline features of the particle in more detail, the IFFT image of the sample was reconstructed (Fig.7(b)). The inset shows the enlarged area of the IFFT image to reveal its characteristics more clearly. The layered structure is easily identified with two lines intercepting the points of the image, making a  $67.19^\circ$  angle.

This area was further zoomed to measure the dimensions of the lattice more accurately. As it can be observed from Fig.7c, the particle has a layered structure comprising stretched points which the distance between them in every layer is 294 pm, while the length of points in alternate layers wherein points are exactly repeating in one direction is 701 pm, according to line profiles in Fig.7e and d, respectively. These parameters are highly compatible with the distance between the two closest carbon atoms if regarded as one point to its neighbour point in the graphene layer (284 pm) and the “c” lattice constant of Graphite-2H (675.2 pm), respectively.

Considering the lines angle, and inter/intra-layer distances as well as the alternating repetition of points in layers, one can confidently conclude that this particle has a Graphite-2H structure with ABA stacking order which has been exposed to the electron beam from its side cross-section. Based on this conclusion, the stretched points in Fig.7c are two adjacent carbon

atoms with a 73.5 pm distance. On this basis, the Graphite-2H structure of the GCNP sample with p63/mmc symmetry is schematically represented in Fig.7f.

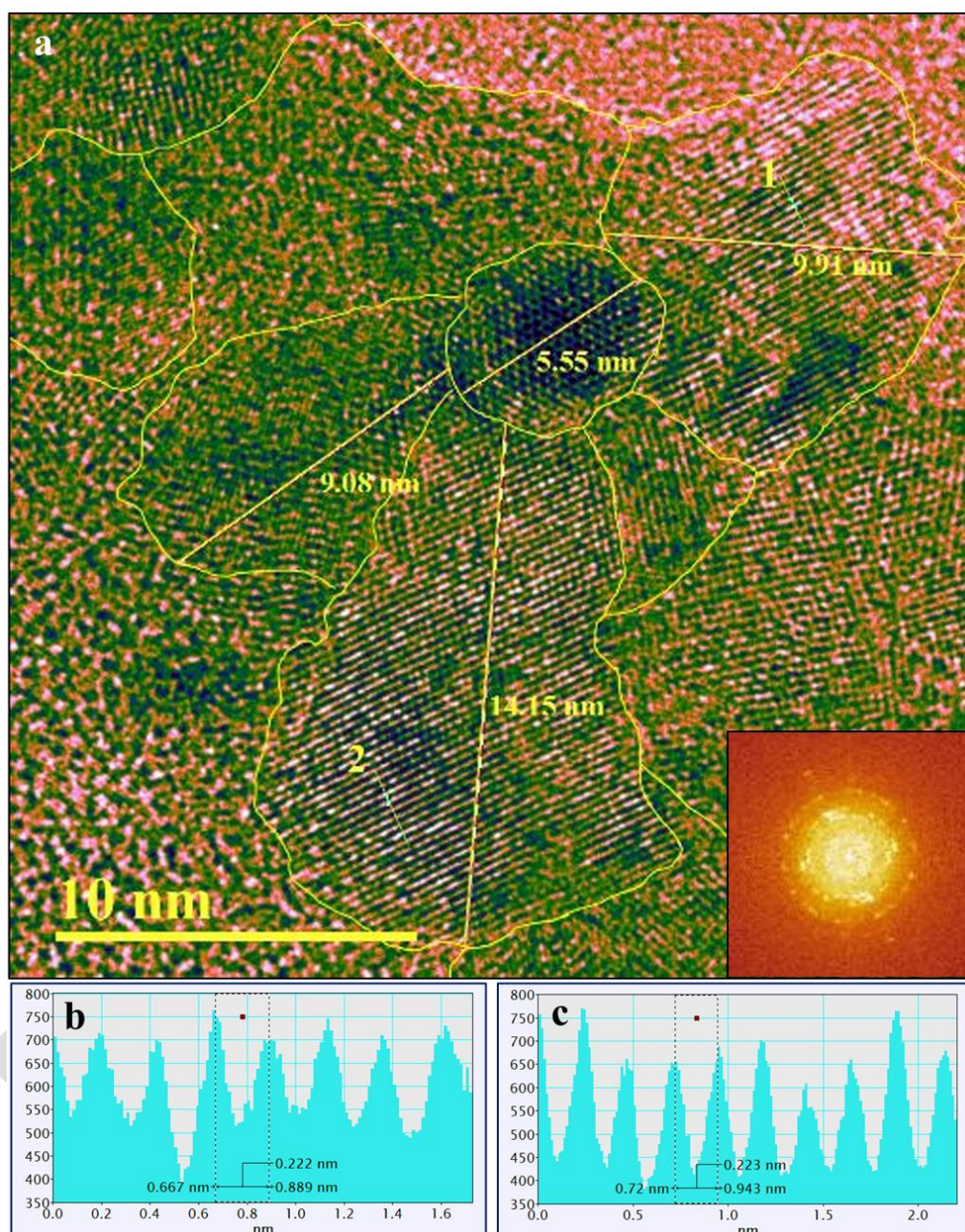


Figure 8. a) A polycrystalline area of GCNP sample with various growth directions. Some of the grain sizes are shown in the picture. The inset shows an FFT image in which multiple spots imply the presence of several crystalline domains in the studied region. Lattice fringes were measured in randomly selected regions which are displayed in b) and c). d-spacings are related to (100) crystalline plane of Graphite-2H structure according to JCPDS card 41-1487.

Due to the presence of narrow rings in the SAED pattern of the sample shown in Fig.3(b), one can deduce that GCNP has polycrystalline areas as well as large crystals. **Fig.8a** shows one of these polycrystalline areas of the sample. Various growth directions of grains with different grain sizes are well recognized in this picture. To identify the crystalline planes of this area, line profiles (b) and (c) from lines 1 and 2 were recorded, respectively. The measured d-spacing of 0.22 nm reveals that the lattice fringes are attributed to (100) planes of graphite structure, according to JCPDS card 41-1487.

Other regions of the sample were also explored by TEM whose results are shown in the following.

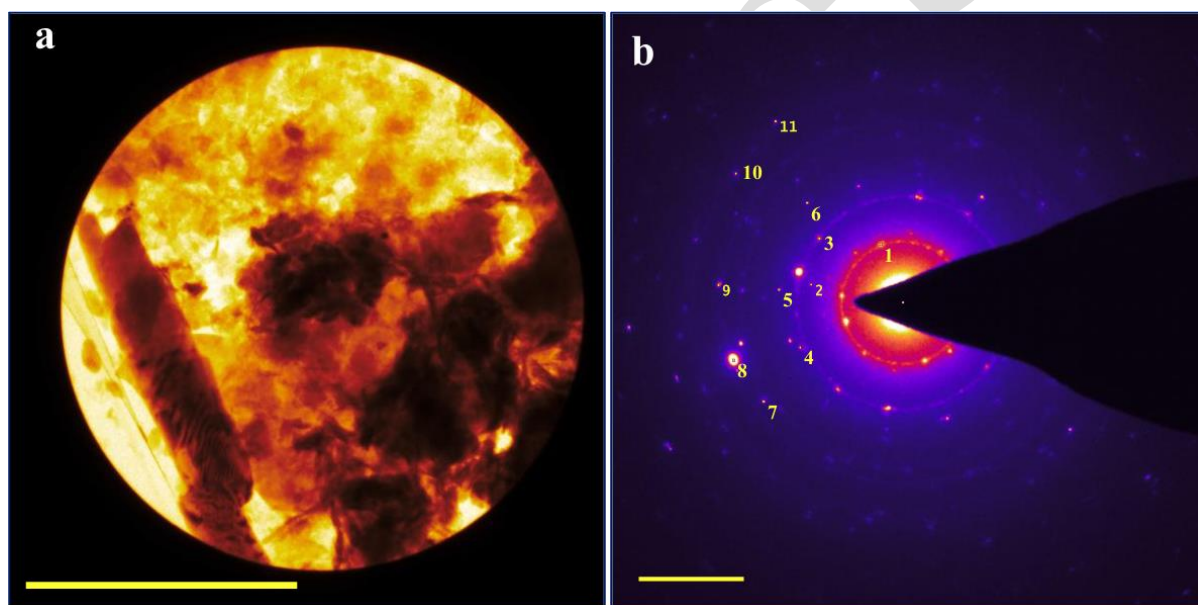


Fig.9. a) and b) TEM and SAED pattern of another region of GCNP sample, respectively. The SAED pattern of (a) comprises of spots, narrow ring and a diffused circle in the centre, indicating the composite nature of the area including large crystals, polycrystalline area and amorphous regions, respectively. Crystalline planes attributed to spots and rings are listed in Table 5.

**Fig.9** shows another region of the GCNP sample explored by TEM. In accordance with the previous region in Fig.3, this area consists of large crystalline domains and polycrystalline particles (spots besides rings in the SAED pattern). However, a diffused circle in the center of

the pattern implies the presence of an amorphous phase as well. These results are in agreement with the XRD pattern of the sample in Fig.2. The presence of spots in the sample shows that crystals with large areas compared to the beam exist in the sample. Respective d-spacings were calculated and listed in **Table 5**.

Table 5. Calculated d-spacings in Fig.9(b) and comparison with Graphite-2H PDF card 41-1487 which resulted in the determination of related crystalline planes. Different green shades represent the difference between the calculated d-spacings of Graphite-2H and the GCNP sample. Dark greens stand for the closest amounts to those of the reference card, while light green is attributed to the larger difference between them.

| Spot | GCNP<br>d-spacing (Å) | Graphite-2H<br>PDF 41-1487 d-spacing (Å) | $\Delta d = d_{\text{Graphite-2H}} - d_{\text{GCNP}}$ (Å) | (hkl)  |
|------|-----------------------|------------------------------------------|-----------------------------------------------------------|--------|
| 1    | 3.385                 | 3.37563                                  | 0.00937                                                   | (002)  |
| 2    | 2.241                 | 2.13865                                  | 0.10235                                                   | (100)  |
| 3    | 1.995                 | 2.03901                                  | -0.04401                                                  | (101)  |
| 4    | 1.861                 | 1.8074                                   | 0.05363                                                   | (102)  |
| 5    | 1.685                 | 1.6811                                   | 0.0039                                                    | (004)  |
| 6    | 1.52                  | 1.54777                                  | -0.02777                                                  | (103)  |
| 7    | 1.226                 | 1.23408                                  | -0.00808                                                  | (110)  |
| 8    | 1.171                 | 1.12084                                  | 0.01062                                                   | (112)  |
| 9    | 1.132                 | 1.05672                                  | 0.01116                                                   | (006)  |
| 10   | 0.9952                | 0.9924                                   | -0.02431                                                  | (202)  |
| 11   | 0.9481                | 0.903685                                 | -0.0443                                                   | (114)* |

\*This peak is not available in PDF card 41-1487. It was introduced in ref <sup>[40]</sup>.

Compared to JCPDS card 41-1487, it is obtained that the sample has a Graphite-2H structure which consists of graphene layers with honeycomb structure stacked on each other with ABA sequence. “A” and “c” unit cell constants were also calculated which results are shown in **Table 6**.

Table 6. Calculated lattice constants for GCNP studied area calculated from data in Table 5.

| plane | GCNP<br>d-spacing (nm) | Graphite-2H<br>(PDF 41-1487)<br>“a” lattice<br>constant (pm) | Graphite-2H<br>(PDF 41-1487)<br>“c” lattice<br>constant (pm) | GCNP<br>“a” lattice<br>constant (pm) | GCNP<br>“c” lattice<br>constant (pm) |
|-------|------------------------|--------------------------------------------------------------|--------------------------------------------------------------|--------------------------------------|--------------------------------------|
| (002) | 0.3376                 | -                                                            | 675.2                                                        | -                                    | 677.0                                |
| (100) | 0.2252                 | 246.9                                                        | -                                                            | 258.8                                | -                                    |

Comparing lattice constants in this area with those of the previous region (Table 3) as well as SAED patterns of both implies that the explored region in Fig.3 and 9 are completely crystallized to Graphite-2H structure, but the crystallinity of the area investigated in Fig.9 is weaker. Data in Table 6 are also consistent with this conclusion. It can be seen, that unit cell dimensions are a little larger than those in Table 3. This area was further investigated at higher magnifications.

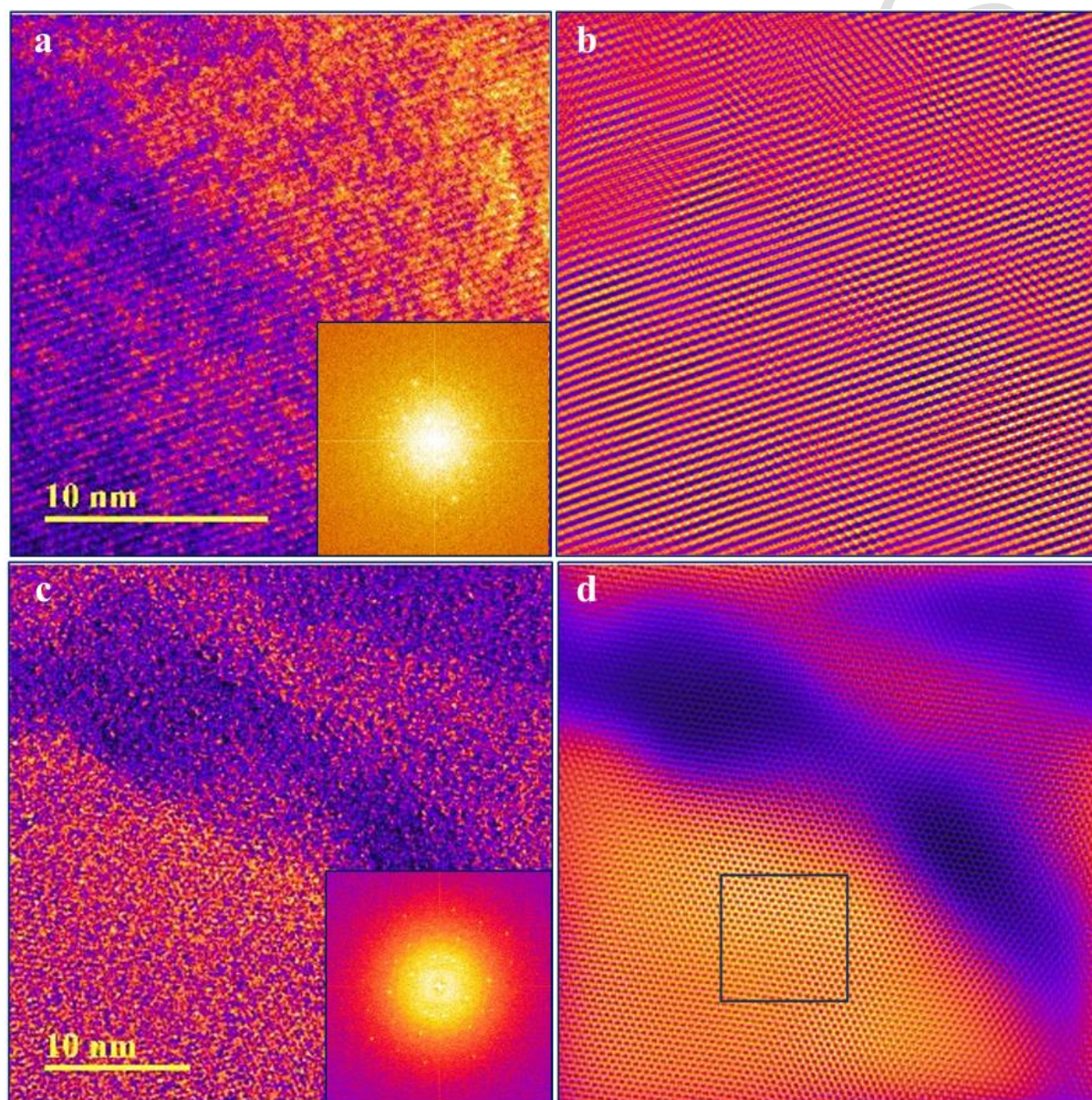


Figure 10. a) to d) Every row shows HRTEM micrographs (left) of two randomly selected regions of the GCNP sample explored in Fig.9, as well as its FFT pattern (inset) and simulated IFFT images (right) showing the ordered structure of the sample. e) The enlarged area of the image(d) of the boxed region, illustrating the highly ordered honeycomb structure with doubled dimensions of that of graphene according to the measured line profiles 1 and 2 shown in (f) and (g), respectively. The inset shows the simulated basal plane structure with respect to the IFFT

image. Green points are those carbon atoms that are apparently detected in the IFFT pattern. However, the stretched vertices may be the result of the appearance of two adjacent carbon atoms boxed in violet ovals. h) IFFT image of image(c) simulated with 6 spots preferably selected from the FFT pattern displayed in the inset of (c), to unveil the hidden perfect graphene structure which was not observable by all spots masking of the FFT pattern. The enlarged area is shown in (i). Measured dimensions are the same as graphene which are displayed in (j) and (k) from the lines 1 and 2, respectively.

**Fig.10** shows two other regions of the sample in Fig.9, which were randomly selected. These areas show highly ordered zones which result in the appearance of spots and a diffused circle in the middle of FFT patterns which indicates the existence of a disorder area. The corrugated pattern seen in Fig.10a was simulated to reveal its crystalline part by choosing spots in the FFT image. Fig.10(b) shows the obtained IFF image wherein the highly symmetric nature of the area is seen. The other micrograph (Fig.10c) with remarkably more spots in its FFT pattern, as well as a smaller diffused circle (the inset) compared to Fig.10a indicates the higher crystallinity of this domain.

A simulated IFFT image of this area (Fig.10d) was also produced. To display its high symmetrical features, the boxed region with the dark blue rectangle was enlarged and displayed in Fig.10e. One can obviously recognize the highly ordered honeycomb structure with stretched vertices and doubled dimensions of the graphene structure of this image. Dimensions were recorded as 506 pm and 270 pm which are double amounts of “a” lattice constant and C-C distance related to the graphene structure, respectively. The inset shows the reconstructed structure of this area with respect to the basal plane of graphite which unveils the hidden atoms of the structure.

Considering three fused carbon rings containing 13 atoms of carbon, only 6 atoms are easily attributed to the IFFT image. However, by more precisely looking at the reconstructed IFFT image with respect to the schematic structure, one can conclude that the stretched vertices

are the result of two adjacent carbon atoms' participation in the FFT pattern. Choosing the 0.142 nm spots from the FFT image (inset of Fig.10c), hidden C-atoms were revealed and the combined stretched vertices were separated so that the perfect basal plane of graphite was obtained (Fig.10(h) and (i)). As can be seen from the line profiles (Fig.10(j) and (k)), lattice constants and C-C distance are in close agreement with the graphene sheet.

### 3.3. Nanoreactors network-directed graphitization mechanism

In a typical CVD process for graphene production, a high-purity hydrocarbon gas, hydrogen, a metal catalyst and substrate, and elevated temperatures above 1000 °C are employed. The general mechanism involves the decomposition of gas molecules, adsorption of the resulting species on the metal surface, dehydrogenation, and finally the arrangement of atomic carbon into the  $sp^2$ -bonded honeycomb lattice on the catalyst<sup>[47], [48]</sup>. Some studies have reported catalyst-free CVD of graphene on quartz substrates<sup>[49], [50]</sup>. In these cases, carbon atoms are generated by plasma<sup>[49]</sup> or by reactive oxygen and hydrogen gases<sup>[50]</sup>, adsorbed on the planar quartz surface, and subsequently organized into a hexagonal  $sp^2$  structure. Although these approaches eliminate the catalyst, they still rely on decomposition of precursor molecules to atomic carbon followed by surface-mediated atomic arrangement into graphene layers.

In contrast, the present work demonstrates a fundamentally different route. Structural, microstructural, and chemical analyses of the GCNP sample reveal that carbon coatings formed on the inner wall of the quartz furnace tube, through low-temperature carbonization of nanoporous sulfonated PDVB microspheres, are highly graphitized and even contain completely crystalline regions. This process is a gas-phase method, yet it occurs without any metal catalyst, substrate, high temperature (compared to CVD process or carbonization and graphitization of organic precursors), laser, plasma, or specialized equipment.

The formation mechanism of the GCNP coating differs fundamentally from conventional CVD. Here, the ~~leaving groups~~ evolved species generated during carbonization of porous NGr microspheres transform extensively into few-layer graphite on the furnace wall. Since no external factor assists in decomposing these groups into atomic carbon, the high degree of graphitization must arise from a mechanism other than atomic-level arrangement. Our previous study showed that sulfonated PDVB microspheres provide nanopores that act as nanoreactors, enabling the fusion of benzene free radicals (FBRs) at temperatures as low as 250 °C <sup>[19]</sup>. The spatial confinement imposed by supermicropores and small ink-bottle mesopores (~95% of the total pore volume) ensures that benzene-derived radicals remain confined and undergo fusion within the pores. However, this same confinement restricts radical growth, limiting graphitization within the microspheres themselves and leaving the potential of the nanopore network unexplored.

In this study, we examine the function of the interconnected nanopore network in facilitating macroscale graphitic film formation. The pore architecture—ink-bottle shaped mesopores and supermicropores linked by narrow molecular-scale necks (~0.6 nm) <sup>[19]</sup> —drives a pore blocking/percolation process during pore depletion. As a result, FBRs are not abruptly released into the quartz tube but are delivered with a controlled rate. This structure not only constrains the size of moieties exiting through narrow apertures, ensuring the transport of only small, highly active FBRs, but also regulates their release rate due to the complexity of the network. Such controlled delivery of precursors into the reaction zone parallels strategies in CVD where deliberate regulation of hydrocarbon feed <sup>[51]</sup> or spatial confinement near growth surfaces <sup>[52-54]</sup> leads to enhanced crystallinity. Consequently, the nanopore-guided release mechanism enables the formation of a continuous, highly crystalline graphitic coating on the quartz wall, achieved under conditions far milder than conventional methods.

In **Fig.11**, a schematic of an individual ink-bottle nanopore as a nanoreactor for production of FBRs from decomposing pore walls during carbonization as well as pores network are displayed.

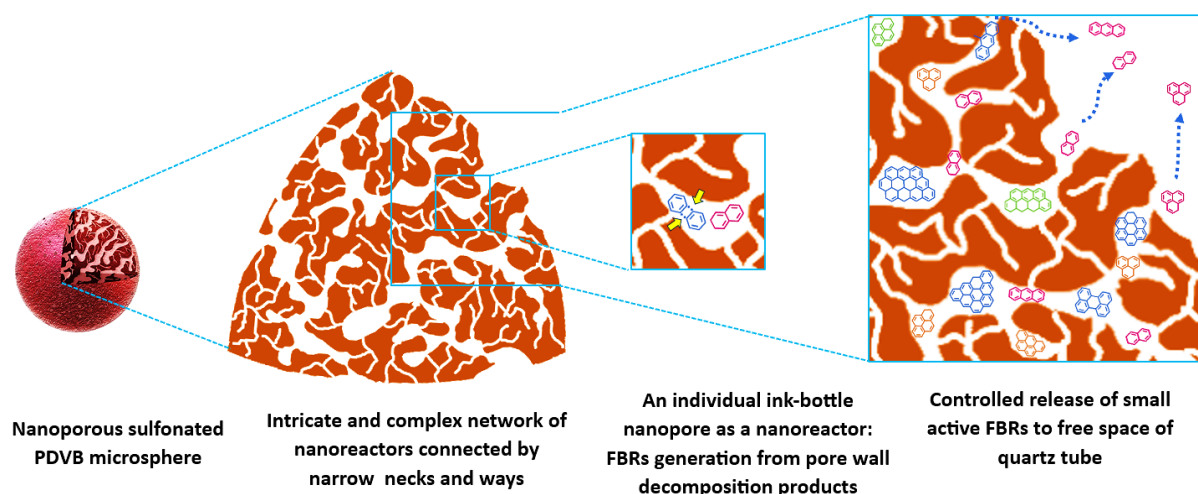


Figure 11. Ink-bottle nanopores in sulfonated PDVB microstructures and their network connected by narrow necks and ways of molecular size resulting in the controlled release of small active fused benzene rings to the quartz tube of the furnace and trapping large moieties inside pores.

Within the large free space of the quartz tube, the released graphitizing moieties—small FBRs—are able to interact and assemble into extended graphitic structures. This growth proceeds laterally through fusion of other FBRs or benzene-derived radicals emerging from the microsphere surface, and vertically via  $\pi$ – $\pi$  stacking onto already-formed FBRs. Evidence for such lateral growth processes was established in our previous study by FTIR and Raman analyses of microspheres heated from room temperature up to 900 °C and 1100 °C <sup>[19]</sup>. Similar observations have been also reported by Roberson and co-workers <sup>[55]</sup> who demonstrated the fusion of polyaromatic hydrocarbons (PAHs, chemically analogous to FBRs) at ~320 °C, while Talyzin et al. <sup>[56]</sup> and Ishii et al. <sup>[57]</sup> documented oligomerization of PAHs below 600 °C. In these cases, thermal energy promotes C–H bond cleavage at PAH edges, enabling polycondensation and the formation of larger aromatic domains.

Taken together, these findings support Nanoreactors network-directed molecular fusion mechanism, distinct from the atomic arrangement pathway of conventional CVD. This mechanism, enabled by the nanoreactor network, governs the formation of highly crystalline few-layer graphite through four sequential steps:

- i) generation of FBRs within the nanoconfined nanospaces of micropores and small mesopores,
- ii) classification of FBRs by the pore architecture so that only small, highly reactive moieties escape into the furnace tube,
- iii) regulation of the release rate by the complex pore network, and
- iv) subsequent lateral growth by in-plane fusion of FBRs and vertical assembly through  $\pi$ - $\pi$  stacking.

Thus, by providing nanoconfined environments to benzene-containing precursors, it becomes possible to enforce their fusion into extended aromatic frameworks, ultimately leading to the growth of graphitic layers. In this pathway, the pore structure itself functions as the critical regulator—synthesizing, filtering, and delivering reactive FBRs into the reaction chamber in a controlled condition. This discovery demonstrates that, independent of extrinsic synthesis parameters such as catalyst, plasma, or high temperature (compared to conventional CVD processes), the intrinsic microstructure of the precursor alone can dictate graphitization. Consequently, the present approach represents a paradigm shift in the synthesis of graphitic carbon, offering a low-cost, scalable route toward crystalline graphene and graphite materials for applications in supercapacitors, batteries, and beyond.

In **Fig.12**, a schematic of the proposed mechanism is illustrated.

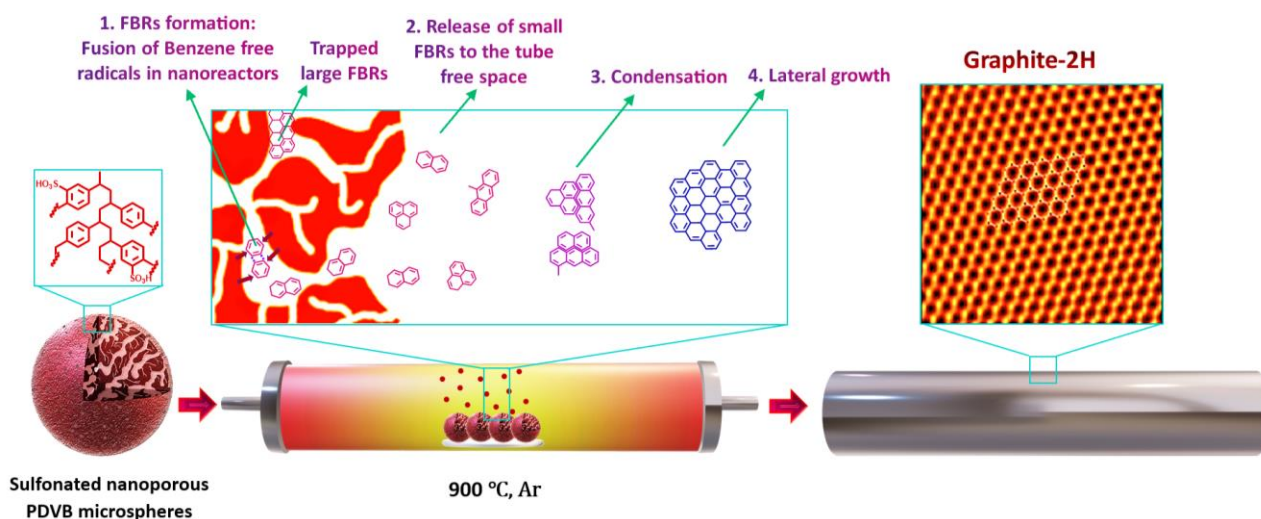


Figure 12. Schematic for the representation of the nanoreactors network-directed molecular fusion mechanism for the formation of crystalline Graphite-2H from carbonization of sulfonated nanoporous PDVB microspheres.

#### 4. Conclusion

In conclusion, we have demonstrated a simple and scalable catalyst-free route for the synthesis of highly graphitized carbon materials through the direct carbonization of nanoporous sulfonated PDVB microspheres in a conventional tubular furnace. The resulting coatings exhibited an average stack height of 69 stacked layers, a graphitization degree of 74%, and the presence of a well-defined Graphite-2H structure with crystalline p63/mmc domains. This process fundamentally differs from conventional catalyst-free CVD approaches, as no substrate, plasma, laser, or reactive gases are required. Instead, the pore architecture of PDVB microspheres functions as nanoreactors that facilitate the fusion and formation of fused benzene rings, their classification, and controlled release to the quartz tube free space, where lateral growth and stacking lead to ordered graphite layers. Our findings introduce a cost-effective and accessible framework for producing graphene/graphite materials, with tunable potential for multilayer graphene synthesis through adjustment of carbonization cycles and thermal treatment.

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## Conflict of Interest

Authors have no conflict of interest.

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