Molecular Dynamic Simulation of Layered Graphene Clusters Formation from Polyimides under Extreme Conditions

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Abstract The previous experimental study illustrated that a direct laser scribing on polyimide (PI) induced the layered graphene, which opened a new door of producing graphene associated materials. However, underlain conversion mechanism is unknown, especially from theoretical perspectives. In this paper, we performed the molecular dynamics (MD) simulation of this mechanism under extreme conditions of the high pressure and temperature which mimic the ones generated by the laser induction. We investigated this process using the ReaxFF potential in a nanosecond time scale. We found out that at a pressure of ~ 3 GPa and temperature of > 2400 K generated from the NVT processes, the layered graphene clusters were crystallized from PI without metal catalysts, which is consistent with the previous experiment. However, if simulated using the NPT processes with a pressure of 27 MPa, the PI were decomposed into small molecules, and no graphene layers were observed. Furthermore, by analyzing the number of the carbon rings and the pair distribution function of them we quantified the crystallinity of the graphene clusters. Through tracing the emission of the small molecules such as H_2O , N_2 , H_2 , CO we propose the possible reaction paths for both of the NVT and NPT processes.

Key words: graphene, polyimide, laser, molecular dynamics

1. Introduction

Materials with atomically layered structures have aroused broad interests from both fundamental science and commercial applications. Graphene, the first widely explored two-dimensional (2D) material, has shown many unique physical and chemical properties [1-3], which make it potential for applications in various fields ranging from the energy storage to the electronics [4-7]. In order to fully utilize such potentials, a production method with a cost-effectiveness, scalability, and good quality control is to be developed. Among a series of methods the chemical vapor deposition (CVD) yields the graphene films with the best quality [8-10]. Understanding its growth mechanism has stimulated various MD simulation work. Meng et al. studied the graphene growth and healing of its defects on Ni surfaces by the ReaxFF potential [11, 12]. It was shown that the Ni atoms could be pulled out of the surface during graphene growth, which hinders the healing of graphene. Lu et al. used the ReaxFF potential to simulate the graphene growth on nickel surfaces from naphthalene and fluorine [13]. It was found that the growth involved the process of the nickel-catalyzed dehydrogenation, ring opening, isomerization, dimerization, and cyclization. Based on these results, an optimum growth temperature was derived. They further found out that without the nickel catalyst, heating of the naphthalene/fluorene only resulted in amorphous carbon. These simulation results indicated the primary role of metal catalysts in the graphene formation under thermally cracking of the hydrocarbon precursors. Despite the progress in this area, it still lacks simulation research on whether graphene layers can be produced from polymers without any metal catalysts.

The posing of this question is due to a recent experimental work of producing layered

graphene materials by a laser scribing on polyimide (PI) films without involving any metal catalysts [14, 15]. The temperature rise in polyimide under laser irradiation is estimated to be ~2700 K as illustrated in supplementary information. It is well known that the laser irradiation on materials can provide a much faster heating rate than the one using a hotplate or a furnace [16]. The rapidly heating by the focused photons deposits much energy on the materials. Thus, the materials don't have enough time to expand or release heat, leading to a localized reaction condition with a high pressure and a temperature. For instance, the laser ablation of silicon generated a spike pressure of 10 GPa and a temperature of 8000 K [17]. These conditions are significantly different from the ones used to grow graphene under the CVD process. We speculate that under such extreme conditions the mechanism of nucleation and defects healing in graphene layers produced from the polymers will be very distinguished. Thus, understanding the physical and chemical processes in this laser-polymer interaction will facilitate a further development of this technology in producing high quality graphene and arise broader interests of laser production of other 2D materials beyond graphene.

In this work, we implemented the MD simulation with the ReaxFF potential in a nanosecond (ns) time scale to study the graphitization process of PI precursors under the canonical ensemble (NVT) which generated a pressure of ~ 3 GPa at the annealing temperatures of 2400 K, 2700 K, and 3000 K. The results showed that PI was crystallized to the layered graphene clusters without metal catalysts. To prove the speculation of the role of the high pressure in the layered graphene formation we also performed isothermal–isobaric ensemble (NPT) under the same temperatures but a much lower pressure of 27 MPa. The results show that

the PI are decomposed to small molecules rather than forming the layered graphene clusters.

2. Simulation Methods

The ReaxFF potential divides the total inter-atomic energy E into several contributions based on the analysis of the inter-atomic electromagnetic field [18-26]. The potential contains the bond energy, lone pair energy, overcoordination and undercoordination energies, valence energy, penalty energy, three-body conjugation energy, torsion angle energy, hydrogen bond energy, van der Waals energy, and Coulomb energy [19, 20]. Each term is parameterized by the density **functional** theory (DFT) calculation. The parameters for C, H, O, N atoms have been used to simulate the shock wave impact of nitramine RDX [19, 20], detonation of triacetonetriperoxide (TATP) [21], disintegration of the Kapton films [22], the pyrolysis of polyacrylonitrile (PAN) [23] and phenolic [24-25], and the combustion of JP-10 hydrocarbon jet fuel [26]. Therefore, the ReaxFF potential has a certain level of accuracy in studying the formation mechanism of layered graphene clusters from PI precursors under the mimicked laser-induced extreme conditions.

The ReaxFF potential integrated in the Lammmps package was used in this work [27]. In all simulations the time step was set to 0.25 femtosecond (fs). The initial system was built in the following steps. First, as shown in Fig. 1 the PI monomers ($C_{22}H_{12}N_2O_5$) were constructed and optimized through the first principle calculation using VAMP package integrated in the Material Studio 7.0 to obtain the equilibrium bond length and angles of the monomers (Fig. S1a). Then, 32 monomers were assigned in a cubic cell with the face-centered cubic (FCC) principle. In all simulations we applied periodic boundary conditions to the cells. The initial cells were slowly

compressed to a density close to an experimental value of 1.308 g/cm^3 . Little deviation from the initial monomers was detected. Then the systems were kept at an equilibrium temperature of 300 K for 40 picosecond (ps) (Fig. S1b).

Figure 1. Scheme of a PI monomer.

After the initialization of systems, we performed both NVT and NPT simulations in this study. When we performed NVT simulations, the systems were firstly heated from 300 K to targeted temperatures (T_p) of 2400 K, 2700 K, and 3000 K in 600 ps. Then they were annealed at the individual T_p for another 600 ps, during which the temperatures were controlled by the Nosé–Hoover thermostat. Finally, the systems were cooled down to 300 K in another 600 ps. Therefore, the total heating-annealing-cooling processes took 1.8 ns (Fig. S1c). In the NPT simulations, the temperature evolution of the heating-annealing-cooling process was the same to the NVT simulations. The equilibrium pressures were controlled at 27 MPa and 0.8 GPa with the Nosé–Hoover barostat. In both NVT and NPT simulations five different initial systems were randomly chosen at different time points during the equilibrating stages (Fig. S1b), and the collected data was averaged over these five trajectories to reduce the statistic errors. The motivation of performing both NVT and NPT simulations is that the laser induction is believed to create a high pressure besides a high temperature, which can be mimicked by the NVT ensemble. In contrast, the conditions of a furnace pyrolysis, in most cases, are close to the

low-pressure NPT ensemble. The comparison simulation results will guide us to better understand the formation mechanism of the layered graphene clusters upon the laser induction on the polymers.

3. Results and Discussion

3.1 NVT simulation and the crystallization process of the graphene clusters

First we carried out the NVT simulations to mimic the heating process generated by the laser induction. Since the volume is kept the constant, upon heating the pressure of the systems will start to increase. Its evolution is presented in Fig. 2. The pressure peaks for $T_p = 2400$ K, 2700 K, and 3000 K are 2.6, 2.9, and 3.2 GPa, respectively. At the annealing stages the pressures are stabilized at ~ 2.4 GPa for all three cases. After the systems are cooled down, the final pressures are reduced to 50 MPa, 50 MPa, and 150 MPa for $T_p = 2400$ K, 2700 K, and 3000 K, respectively, which are close to the values of the initial systems.

Figure 2. Pressure evolution during the NVT process. Solid line: $T_p = 3000$ K, dash line: $T_p = 2700$ K, circle: $T_p = 2400$ K.

The representative snapshots of the final products at $t = 1.8$ ns for $T_p = 2400$ K, 2700 K, and 3000 K are shown in Fig. 3 a-c. To facilitate the observation, the small molecules with the atom numbers ≤ 4 are not displayed in the snapshots. It can be seen that at all three T_p large carbon clusters form. As T_p increases the carbon clusters exhibit more ring structures than chain structures (Fig. 3 a, b). Moreover, they are folded in the 3D space (Fig. 3 a-c), leading to a large specific surface area, which is beneficial to the applications in the energy storage and catalysts [14]. Specifically, the carbon clusters obtained from a representative trajectory at $T_p = 3000$ K exhibit double layered graphene-like structures (Fig. 3c). The interlayer distance of this double layered structure is 0.31 nm, which is almost the same to standard interlayer distance in graphite (0.335 nm). The crystal structures of each layer are shown in Fig. 3 d and e. It can be seen that each layer contains five-, six-, and seven- membered carbon rings. The observed Stone-Thrower-Wales (STW) defects indicated in Fig. 3e agree well the experimental results showing that the obtained laser induced graphene contains a certain amount of heptagon-pentagon defects [14]. Besides, Fig. 3 d, e show that most of the non-carbon atoms such as oxygen and nitrogen are bonded to the edges of graphene layers rather than the planes. It may suggest that these non-carbon atoms could act as the intermediate atoms that assist the formation of the carbon rings. Previous studies showed that the hetero atoms such as N, B and P favored the doping on the edges of graphene layers over the doping on the planes [28-31].

To further study the effect of the T_p on the crystal structures of the graphene layers we quantitatively analyzed the total number of the atoms in the biggest clusters obtained at $T_p = 2400$ K, 2700 K, and 3000 K, respectively (Fig. 4a). The atomic number increases more rapidly

at the higher T_p , indicating that the higher T_p promotes the growth of the clusters. Another

Figure 3. Representative snapshots from the NVT processes. Snapshots of the final clusters obtained under the temperatures of 2400 K (a), 2700 K (b), 3000 K (c), in which the molecules with atom numbers of ≤ 4 are not shown. (d, e) Enlarged views of the layers indicated in c. The STW defects in (e) are marked with the green color. The white atoms represent H, the black atoms represent C, the red atoms represent O, the blue atoms represent N.

observation is that at $T_p = 2700$ K and $T_p = 3000$ K the numbers of the atoms in the maximum clusters reduce after they reach the maximum size. If we combine this observation with Fig. 4b which shows that the number of the carbon atom keeps growing for all T_p , we can conclude that the shrink of the sizes of the clusters in Fig. 4a is due to the removal of non-carbon atoms. In the

cooling stages from 1.2 ns to 1.8 ns, the numbers of H, O, N atoms keep almost constant (Fig. 4 c-e), indicating that the removal of the non-carbon atoms needs to overcome certain energy barriers and is likely to happen at a higher temperature. Thus increasing T_p and simulation duration will prompt the crystallization of the carbon clusters, making the structures closer to the perfect graphene layers.

It is shown in Fig. 4a that at $T_p = 3000$ K the cluster size increases rapidly in the beginning of annealing stage. We further investigate the molecular configurations by looking at the representative snapshots in the period from 600.3 ps to 601.25 ps, as shown in Fig. 5. Fig. 5 shows that small ring clusters are bonded with the assistance of N (Fig. 5a and b) and O (Fig. 5c and d) radicals, which are produced from the decomposition of initial PI monomers. These heteroatoms may have catalytic effect on the fast growth of large clusters (Fig. 4a). They will be then slowly removed as the annealing stage goes, resulting in the improved crystallinity of graphene-like clusters.

Figure 4. Elemental analysis in the biggest clusters resulted from the NVT processes. (a) Number of total atoms; (b) carbon atoms; (c) hydrogen atoms; (d) oxygen atoms; (e) nitrogen atoms. Numbers of atoms were averaged over 5 trajectories.

Figure 5. Snapshots from one trajectory of the NVT processes at $T_p = 3000$ K at 601.25 ps (a), 601.30 ps (b), 600.25 ps (c), 600.30 ps (d). In a-d the distances between two atoms marked by the arrow are 4.11, 1.53, 2.36, and 1.62 Å, respectively. The white atoms represent H, the grey and green atoms represent C, the red atoms represent O, the blue atoms represent N.

Figure 6. Evolution of the carbon rings in the NVT processes under different annealing temperatures. $T_p = 2400$ K (a), $T_p = 2700$ K (b), $T_p = 3000$ K (c). The green line represents hexagons (6MR), the blue line represents pentagons (5MR), the red line represents heptagons (7MR), and the dark dash line represents 2D connected hexagons (6MRC). The numbers of the carbon rings were averaged over 5 trajectories.

We further analyzed the carbon rings obtained at T_p of 2400 K, 2700 K, and 3000 K (Fig. 6). At all T_p the number of 6-membered rings (hexagons) in the original PI precursors decreases from 96 to ~ 25 during the heating stages. Simultaneously, the numbers of 5-membered rings (pentagons) increases from zero to > 50 , which may suggest that the formation of pentagons origins from the hexagons. Both of these processes happen at the same time of $t = 540$ ps, 430 ps, and 400 ps for $T_p = 2400$ K, 2700 K, and 3000 K, respectively. At these points, the systems are exactly heated to ~ 2100 K which is suggested to be the minimum temperature of opening the hexagons. Right from these points, all 5-, 6-, and 7- membered rings (heptagons) start to increase, indicating the initialization and of crystallization process in the carbon clusters. At $T_p = 3000$ K the hexagons significantly boost, which suggests that the higher thermal energy would promote the formation of the hexagons inside the clusters and make their structures closer to the graphene (Fig. 6c). Fig. 6c also shows that during the simulation duration the numbers of the heptagons and pentagons are stabilized. The appearance of heptagons and pentagons agrees with the DFT calculation [32] which showed that without metal catalysts the growth of heptagon-pentagon could be more energetically favorable than hexagons. We also separately investigate the evolution of 2D connected hexagons (having at least one neighboring 2D connected hexagons) and the isolated hexagons (having no neighboring 2D connected hexagons) at T_p of 2400 K, 2700 K, and 3000 K. The results are shown by the dark dash lines in Fig. 6. A higher percentage of 2D connected hexagons indicates a better graphene-like crystallinity. It can be seen that the initial systems have no 2D connected hexagonal rings. After the NVT processes, the percentage of 2D connected hexagons in the final systems increases from 58.8% at $T_p = 2400$ K to 95.6% at $T_p = 3000$ K, which

indicates the increased graphene-like crystallinity.

To quantify the crystallinity of the graphene clusters we employed the radial distribution function (RDF), $G(r)$, which describes the chance of finding an atom at a certain distance from a targeted atom. We only consider the RDF among carbon atoms. The RDF of a single layer graphene (SLG) is presented as a reference, which shows several discrete peaks, labeled as 1st, 2nd, 3rd, and 4th (Fig. 7a). They correspond to the distances of 1.42, 2.46, 2.84, and 3.76 Å. The 4th peak in RDF of SLG represents the interatomic position of neighboring rings (Fig. 7a). Therefore, the rising of the 4th peak of RDF can be regarded as an indication of the formation of honeycomb rings. The RDFs of the carbon clusters obtained at $T_p = 2400$ K, 2700 K, and 3000 K are shown in Fig. 7b, c. Fig. 7c shows that as the T_p increases, the intensity of all the 1st, 2nd, and 4th peaks in the RDFs gets larger and larger, indicating that the crystal structures are closer and closer to the SLG. Another indication of the hexagons in the graphene is the 3rd peak in the RDF.

Figure 7. RDF analysis of the carbon rings obtained from the NVT processes. (a) Scheme of the peaks in the single layer graphene (SLG); (b) RDF analysis of the final carbon clusters under different T_p ; (c) Enlarged view of the area indicated in (b); (d) RDF analysis of the carbon clusters obtained under $T_p = 3000$ K at different simulation durations; (e) Enlarged view of the area indicated in (d). The collected data was averaged over 5 trajectories. “p1”, “p2”, “p3”, “p4” in (b-e) refer to the 1st, 2nd, 3rd and 4th peaks.

As shown in Fig. 7c it start to appear in the carbon clusters obtained at $T_p = 3000$ K, indicating an increased crystallinity. To better investigate this crystallization process we plot the evolved RDFs

of the clusters obtained at $T_p = 3000$ K (Fig. 7d, e). Before the heating stage the RDFs show the 1st and 2nd peaks because each PI monomer has three carbon hexagons (Fig. 7d). Fig. 6e shows that at $t = 600$ ps, the intensity of the 2nd peak is smaller than that at $t = 0$ ps. It indicates that a large amount of the 6-membered rings in the original PI monomers are opened, which agrees with the ring analysis shown in Fig. 6c. At $t = 1200$ ps the 2nd peaks are re-established and the 4th peaks evidently rise, suggesting the increased crystallinity as the simulation duration increases.

Other than analyzing the carbon clusters, we also studied the generated small molecules (atomic number ≤ 4) at $T_p = 2400$ K, 2700 K, and 3000 K (Table 1). The evolution of these molecules is plotted in Fig. S2. The molecular gases containing the N atom are N_2 , NH_3 , and HCN. But N_2 composes the main product of the N atom in the final configurations. Moreover, the increased T_p doesn't produce more NH_3 and HCN. It can be inferred that the NH_3 and HCN could play roles of intermediate products, which are first generated as the dissociation of N groups from the clusters and then converted to N_2 . Other main products of small molecules from non-carbon atoms include H_2O , H_2 , as shown in Table 1. The H_2O and H_2 molecules dominate in the final gases, and their amounts prominently increase as T_p increases. Furthermore, as the T_p increases more non-carbon atoms are removed from the precursors, indicating the higher crystallinity of the carbon clusters. It agrees well with the previous cluster analysis that the carbon clusters obtained under a higher temperature have much less non-carbon atoms (Fig. 4). Some carbon atoms exist as the final forms of CO and CO_2 . But as T_p increases their amounts have no significant change, suggesting that the high pressure suppresses the further decomposition of the polymer precursors into small molecules. **There are very few carbon dimers**

observed in the final products of all NVT processes. But a small amount of them are observed during the annealing stage (Fig. S3). Therefore, we suppose that these carbon dimers are the products of PI decomposition in the heating stage. In the annealing stage, they are quickly reacted and connected to bigger carbon clusters. It is quite different from the case in the NPT processes in which the carbon dimers are among the main final products.

Table 1. Comparison analysis of the total numbers of the small molecules (atoms number ≤ 4) in the volatile gases and the atomic percentage of the individual elements present in them after 1.8 ns NVT and NPT simulations. The collected data was averaged over 5 trajectories.

	NVT			NPT		
T_p	2400 K	2700 K	3000 K	2400 K	2700 K	3000 K
H₂O	41	72.4	92.6	6.2	4.6	2.8
CO	4.4	4.8	6.8	140.6	148.8	153.6
CO₂	9.6	6.2	4.4	0.4	0.4	0
H₂	16.6	32	37	77.4	141.6	157.6
HCN+CN	1.6	3	2.8	54.6	59.2	61.4
NH₃	4.4	4.8	5.6	0.2	0.2	0
N₂	3	10.2	16.4	0.4	1.4	0.8
HC₂+C₂	0	0	0	148.8	216.8	229.6
C%	2.23	1.99	1.99	70.26	91.39	96.02
H%	33.85	58.91	72.60	64.53	93.64	97.86
O%	40.41	56.00	67.62	92.37	96.49	97.87
N%	18.75	44.06	64.37	87.17	97.80	98.74

To summarize the previous analysis of NVT simulation, we can expect the possible

crystallization process in the following procedure. First, the 6-membered rings in the original PI precursors are opened due to the high thermal energy. Most of them form the 5-membered rings and the carbon dimers. And a few gases molecules like HCN, CO and CO₂ are generated. Simultaneously, the non-carbon atoms such as H, O, and N are stripped out of the precursors and form H₂, H₂O, N₂, and NH₃. The high pressure suppresses the further decomposition of the carbon rings into small gaseous molecules. It also promotes the generated carbon dimers or small carbon clusters to be bonded to opened rings of the existing larger carbon clusters composed of 5-, 6-, and 7- membered rings upon the catalysis of the heteroatoms such as N and O. The high thermal energy heals the defects inside the graphene clusters. Thus, the longer simulation duration and higher T_p would facilitate the crystallization of the graphene clusters.

3.2 NPT simulation and the role of pressure

Fig. 2 shows that in the NVT simulation the pressure can rise to 3.2 GPa during the heating stages. We suspect that such a high pressure could be the main attribution to the crystallization of the layered graphene clusters from the polymers without the metal catalysts. To verify such a hypothesis, we also performed the NPT simulations. The temperature evolution was the same to the NVT simulations (Fig. S1c). We then maintained the pressures at a relatively lower value of 27 MPa and a relatively higher value of 0.8 GPa to compare the final products. The data were averaged over five equilibrium initial systems.

The NPT simulation allows the volume to expand. The average volumes can be calculated from the snapshots of the final systems. They are (3.6 nm)³, (3.9 nm)³, and (4.0 nm)³ for $T_p =$

2400 K, 2700 K, and 3000 K, respectively, at an equilibrium pressure of 27 MPa. In contrast, all NVT systems have a constant volume of $(2.5 \text{ nm})^3$. The snapshots of the NPT simulation show that the final configurations consist of all small carbon chains and gaseous molecules (Fig. 8). The ring analysis shows that almost no rings are formed (Fig. S4). It further confirms that the rings in the precursors are irreversibly broken and cannot be re-generated to form the graphene layers under the low pressure.

Figure 8. Snapshots of the final clusters obtained from NPT processes under different annealing temperatures. (a) 2400 K; (b) 2700 K; (c) 3000 K. The white atoms represent H, the black atoms

represent C, the red atoms represent O, the blue atoms represent N.

The small molecular byproducts and the concentration of their elements at $T_p = 2400$ K, 2700 K, and 3000 K are summarized in Table 1. The molecules obtained from NPT simulations are quite different from the NVT simulations. The main forms of O and N in the volatile gases are CO, CN, and HCN, while in the NVT simulations the main forms of O and N are H_2O and N_2 . For example, in the NPT processes with $T_p = 3000$ K a small concentration ($N_{H_2O} = 10$) of H_2O , generated from the decomposition of PI, is observed. It steadily decreases during the whole annealing stage, and keeps constant during the cooling stage (see Fig. S5). Another significant difference from the NVT processes is that the volatile gases are composed of a larger concentration of the carbon atoms. In addition to HCN, CN, and CO, a considerable amount of the carbon atom exists as C_2 and HC_2 . Theoretical studies indicate that these carbon dimers are the dominant feeding species in the epitaxial growth of graphene on Cu surfaces [33-35]. Although the decomposition of PI at the low pressure produces the carbon dimers, they cannot be crystallized into graphene-like structures without a presence of the high pressure or metal catalysts. The amount of H_2 generated from the NPT processes is much higher than that from the NVT processes (Table 1). Moreover, the increase of CO and H_2 concentrations during the annealing stages matches the decrease of H_2O concentration (Fig. S6). It may suggest that H_2O and N_2 can easily react with the carbon under the NPT conditions. Compared with NVT processes, these distinguished results are due to the relatively lower pressures, under which the reactions favor the following paths when the systems are kept at the high temperatures:

These processes rapidly happen after 400 ps (Fig. S6). The production rates of the gaseous molecules evidently increase with the increased T_p . At $T_p = 2700$ K and 3000 K, their concentrations reach a plateau before the ends of the annealing stages. It suggests that the reaction is almost complete and reaches an equilibrium in the simulation duration. This result can be also inferred from Table 1 showing that as T_p increases from 2400 K to 3000 K, the concentrations of all the elements in the small molecules increase close to 100%. **These results are significantly different from the ones obtained from the NPT simulations performed at a higher pressure of 0.8 GPa under the same temperature of 3000 K (Fig. S7). Fig. S7 shows that the time evolution of 5-, 6-, 7-membered ring is very similar to the cases shown in NVT processes, indicating the formation of a considerable amount of carbon clusters (Fig. 6). This good agreement further confirms the important role of high pressure in forming the graphene-like clusters.**

4. Conclusion

In this work the formation process of the layered graphene clusters from PI without the presence of the metal catalysts was investigated by the MD simulation. In the NVT ensemble, the raised temperature of > 2400 K will create pressures of > 3 GPa in the heating and annealing stages. The graphene clusters can be obtained at such conditions. The RDF and ring analysis show that the crystallinity of them is improved with the increased temperatures. The chemical analysis shows that in all NVT simulations the carbon element rarely exists in the volatile gases,

while other non-carbon elements are significantly removed as the volatile gases. The results from the NPT simulations are significantly different from the NVT cases. No graphene clusters are observed in the final configurations. Chemical analysis shows that the carbon elements exist as the forms of CO, HCN, and other carbon dimers under the high temperatures. The reason for such a distinction is that the high reaction pressure suppresses the decomposition of the PI precursors and promotes carbon dimers or smaller carbon clusters to be continuously bonded into the larger graphene clusters.

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