Substrate-free microwave synthesis of graphene: experimental conditions and hydrocarbon precursors

Albert Dato\textsuperscript{1,3} and Michael Frenklach\textsuperscript{2,3}

\textsuperscript{1} Applied Science and Technology Graduate Group, University of California, Berkeley, CA 94720, USA
\textsuperscript{2} Department of Mechanical Engineering, University of California, Berkeley, CA 94720-1740, USA
E-mail: amdato@me.berkeley.edu and myf@me.berkeley.edu

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Abstract. The effects of applied microwave power, gas flow rate and precursor composition on the substrate-free gas-phase synthesis of graphene were investigated. Graphene was produced through the delivery of ethanol droplets into argon plasmas, and a decrease in the flow rate of the gas used to generate the plasmas resulted in the formation of graphitic particles and bulk graphite structures. Carbonaceous soot particles were created by delivering isopropyl alcohol into the reactor, while no solid matter was created from methanol. Increasing the applied microwave power was found to have no effect on the structures of the synthesized materials. These findings indicated that the synthesis of graphene in the gas phase was the result of the slow inception and extremely fast growth of aromatic nuclei in the plasma afterglows.

\textsuperscript{3} Authors to whom any correspondence should be addressed.
1. Introduction

Graphene, a single layer of carbon atoms tightly packed in a two-dimensional (2D) honeycomb lattice, is a novel material that possesses unique electrical, mechanical and thermal properties \[1\]–\[3\]. Graphene research has intensified since the material was first isolated in 2004 \[4\], and this has stimulated the development of numerous graphene synthesis techniques, such as the chemical exfoliation of graphite \[5\]–\[7\], growth on substrates by epitaxy \[8, 9\] and chemical vapor deposition (CVD) \[10\]–\[12\].

Free-standing graphene has been created without the use of substrates or graphite for the first time through gas-phase microwave synthesis \[13\]. Aerosols consisting of argon gas and liquid ethanol droplets were delivered directly into argon plasmas that were generated using an atmospheric-pressure microwave plasma reactor. Ethanol droplets evaporated and dissociated in the plasmas over a time scale of the order of \(10^{-1}\) s and formed graphene that exhibited a highly ordered, oxygen-free structure \[14\]. In contrast to alternative approaches, this technique is capable of rapidly and continuously synthesizing ultrahigh-quality graphene in a single step at ambient pressure. However, in the microwave synthesis study cited above, graphene was essentially produced under a single set of experimental conditions \[13\]. In the present study, we investigate the effects of the applied microwave forward power (MFP), precursor composition and gas flow rate on the gas-phase synthesis of graphene. The results presented in this work also shed light on mechanistic features of the gas-phase process.

2. Experimental details

Experiments were conducted in a commercially available (MKS/ASTeX AX2518) atmospheric-pressure microwave plasma reactor. A diagram showing the main components of the reactor is presented in figure 1. A microwave power supply chassis-generated dc power for the magnetron tube housed in the remote magnetron head. The remote magnetron head was capable of
generating MFPs of 180–1800 W at a frequency of 2.45 GHz. The MFP was varied using an analogue power controller connected to the microwave power supply chassis. Microwaves generated by the remote magnetron head were directed through a wave guide towards the atmospheric-pressure plasma torch. The wave guide passed through four components that were designed to protect the magnetron from reflected microwaves: a precision power detector, an impedance matching device, a three-port circulator and a dummy load. The precision power detector measured forward and reflected microwave power and communicated in a feedback loop with the impedance matching device. The impedance matching device automatically adjusted impedance matching stubs to reduce the power of microwaves that were reflected back towards the remote magnetron head. The three-port circulator was located directly in front of the remote magnetron head. This component diverted the reflected microwaves towards the dummy load, which was designed to absorb reflected microwave energy.

Synthesis reactions took place in the atmospheric-pressure plasma torch. A photograph and a simple diagram of the torch are given in figure 2. A quartz tube located within the torch was used to pass an argon gas stream through a microwave guide. This stream, hereafter called plasma gas, was used to generate argon plasmas. A smaller alumina tube, which was positioned concentrically within the quartz tube, was used to deliver an aerosol consisting of argon gas and liquid precursor droplets directly into the plasmas. This tube terminated directly below the central region of the torch where electrons in the ionized plasma gas coupled with the applied microwaves, hereafter called the coupler region. For all experiments, the aerosol flow rate was set to 2.4 and $4.0 \times 10^{-4}$ liters per minute (lpm) for argon gas and precursor droplets, respectively.

Solid reaction products synthesized in the torch were collected on nylon membrane filters downstream from the plasma. Materials were removed from the filters and sonicated in ethanol for 30 s. Droplets of the sonicated suspensions were deposited on lacey carbon grids for transmission electron microscopy (TEM) imaging and electron energy-loss spectroscopy (EELS) analysis. TEM images and EELS spectra were obtained using a 200 kV Philips CM200/FEG transmission electron microscope equipped with a Gatan imaging filter. The synthesized sheets were also characterized by Raman spectroscopy using a SPEX 1877 0.6 m triple spectrometer at 488 nm, with a $5 \text{ cm}^{-1}$ spectral resolution. Specimens for Raman
characterization were prepared by scraping the as-synthesized materials from the filters and depositing the samples directly onto a 1 cm$^2$ silicon substrate.

The effects of MFP and precursor atomic composition were investigated over an MFP range of 250–1050 W. Experiments were conducted at 200 W intervals. Liquid ethanol, methanol and isopropyl alcohol (IPA) droplets were delivered into argon plasmas at each MFP setting. The plasma gas flow rate was fixed at 6.8 lpm for this series of experiments.

The mechanistic implications of the experimental investigation, as will be discussed below, suggested that graphene synthesis could be achieved by using an organic compound with a similar atomic composition to that of ethanol. On the basis of this, we investigated the delivery of dimethyl ether (DME) into the reactor. Ethanol and DME have the same atomic composition ($C_2H_6O$), but DME does not contain a C–C bond as ethanol does. DME was delivered into the reactor at an MFP of 250 W and a plasma gas flow rate of 6.8 lpm. The flow rates of argon and DME were set to 2.4 and $4.0 \times 10^{-4}$ lpm, respectively. Although the volumetric flow rate of DME was similar to that of ethanol, the mass flow rate of $C_2H_6O$ into the reactor was smaller because DME was delivered in the gas phase. Gaseous DME and liquid ethanol have densities of 1.97 and 789 g l$^{-1}$, respectively. DME could have been delivered at 0.16 lpm to achieve a similar mass flow rate, but this would have changed the residence time of the precursors and reactive species in the reactor. Therefore, the lower flow rate was chosen to keep the reactor conditions similar to those of the ethanol experiments.

The effect of the plasma gas flow rate was studied by delivering ethanol droplets into the reactor over an MFP range of 250–1050 W. Experiments were also conducted at 200 W intervals. At each MFP setting, the plasma gas flow rates were set to 3.4 and 1.7 lpm, corresponding to 50 and 25% of the initial flow rate of 6.8 lpm, respectively.

3. Results

3.1. Delivery of ethanol at a plasma gas flow rate of 6.8 lpm

Graphene was produced through the delivery of ethanol at every MFP setting investigated. Low-magnification TEM images of the materials produced at 450, 650, 850 and 1050 W are

Figure 2. A photograph and a diagram of the atmospheric-pressure plasma torch.
Figure 3. Low-magnification TEM images of graphene sheets obtained through the delivery of ethanol at MFPs of (a) 450 W, (b) 650 W, (c) 850 W and (d) 1050 W. Scale bars: 100 nm.

shown in figure 3. The synthesized sheets were typically folded, scrolled or overlapping and were similar to the graphene obtained at 250 W [13].

The number of layers in a graphene sheet could be determined by analyzing its folded regions at higher magnification [13, 15, 16]. Folded regions are locally parallel to the electron beam, and single-layer graphene has been found to exhibit one dark line, similar to TEM images of single-walled carbon nanotubes [13, 15, 16]. Bilayer and few-layer graphene sheets exhibit multiple dark lines, similar to TEM images of double- and multi-walled nanotubes, respectively [13, 15, 16]. High-magnification images of the synthesized sheets exhibited single dark lines that are characteristic of single-layer graphene (figure 4).

The graphene EELS spectrum in the carbon K-edge region has been shown to be similar to the spectrum exhibited by graphite [13]. The main features of graphene and graphite spectra are a peak at 285 eV that corresponds to electron transitions from the K-shell to empty $\pi^*$ states and a peak at 291 eV that corresponds to transitions from the K-shell to $\sigma^*$ states [13], [17]–[19]. EELS spectra corresponding to each of the high-magnification TEM images exhibited 1s-$\pi^*$ and 1s-$\sigma^*$ peaks at 285 and 291 eV, respectively, showing that the sheets possessed $sp^2$-bonded structures (figure 4).

The rounding of the peak at 291 eV at higher MFPs is not due to an increase in the MFP but rather to the amount of time it took to obtain a clear, focused image of a single-layer graphene sheet followed by an informative EELS spectrum. Single-layer graphene sheets rapidly become
amorphous when exposed to an electron beam with an accelerating voltage of 200 kV. Some of the graphene EELS spectra shown in figure 4 exhibited sharper peaks because the spectra were obtained at much shorter durations of time after their corresponding TEM images were taken.

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Raman spectroscopy confirmed that the synthesized materials consisted of single-layer graphene. Samples obtained at every MFP setting exhibited D and G peaks positioned at 1350 and 1580 cm$^{-1}$, respectively (figure 5(a)). Furthermore, the sheets had single, symmetric 2D peaks (figure 5(b)) that are characteristic of single-layer graphene [15, 20, 21]. The edges of graphene sheets are always seen as defects, and the presence of the D peak in each of the spectra could be attributed to the many sheet edges captured by the 300 µm × 120 µm Raman laser spot.

Although the MFP did not have an effect on the structures produced in the reactor, the production rate of graphene did noticeably increase with MFP. Graphene was synthesized at a rate of 2 mg min$^{-1}$ at 250 W, and the production rate tripled at 1050 W.

### 3.2. Delivery of methanol

Solid matter was not produced when aerosols consisting of liquid methanol droplets and argon gas were sent into the plasma reactor. No materials were found on the nylon membrane filters in the MFP range investigated.

### 3.3. Delivery of isopropyl alcohol

Dark, carbonaceous particles were produced through the delivery of IPA at every MFP setting. Particles produced at 250, 650, 850 and 1050 W are shown in figure 6. The particles were typically less than 100 nm in diameter and nearly spherical in shape. They were fused together.
Figure 6. Low- and intermediate-magnification TEM images of carbonaceous particles synthesized through the delivery of IPA at MFPs of (a, b) 250 W, (c, d) 650 W and (e, f) 1050 W. Scale bars: (a, c and d) 100 nm and (b, d and f) 10 nm.
Figure 7. High-magnification TEM images and corresponding EELS spectra of soot particles synthesized through the delivery of IPA at MFPs of (a, b) 250 W, (c, d) 650 W and (e, f) 1050 W. Scale bars: 2 nm.

Isolated individual particles were very rarely observed.

High-magnification images revealed that the particles comprised randomly oriented stacks of graphene planes and amorphous domains (figure 7). The synthesized particles thus had characteristics that have been widely reported for carbonaceous soot formed in the...
Figure 8. Raman spectra of soot particles synthesized at increasing MFP. (a) D and G peaks positioned at \( \sim 1360 \) and \( \sim 1600 \) cm\(^{-1}\), respectively. (b) 2D peaks.

combustion and pyrolysis of hydrocarbon fuels [22]–[26] and commercially available carbon blacks [27]. EELS provided further evidence that the particles were soot. Soot exhibits a disordered structure that is an intermediate between graphite and amorphous carbon [27], and EELS spectra for these particles in the carbon K-edge region typically have a sharp 1s-\( \pi^* \) peak and a rounded 1s-\( \sigma^* \) peak [27]. Each of the EELS spectra corresponding to the high-magnification images (figure 7) showed a sharp 1s-\( \pi^* \) transition peak at 285 eV and a rounded dome at 291 eV.

Raman spectroscopy supported the TEM and EELS results. Similar structures were produced in all of the MFP conditions investigated, and thus Raman spectra were acquired only from the particles synthesized at 250 and 1050 W. Soot particles typically exhibit D and G bands that are much wider than the peaks exhibited by graphene and a G peak that is up-shifted to \( \sim 1600 \) cm\(^{-1}\) [28]–[31]. As shown in figure 8(a), the D and G peaks of the particles synthesized at 250 W were broad and positioned at \( \sim 1360 \) and \( \sim 1604 \) cm\(^{-1}\), respectively. The spectrum obtained from the particles produced at 1050 W was similar, with wide D and G peaks positioned at \( \sim 1356 \) and \( \sim 1597 \) cm\(^{-1}\), respectively. The shapes and positions of the D and G peaks for the synthesized particles thus matched the Raman spectra of hydrocarbon soot and commercially available carbon blacks [28]–[31].

The shape and position of the Raman 2D peak widens as the degree of disorder in a graphitic sample increases [32, 33]. For example, disordered soot particles transform into graphitic particles when annealed at high temperatures [33]. Soot was shown to have a wide 2D peak at 2700 cm\(^{-1}\), and the peak became thinner and sharper for the more ordered graphitic particles [33]. The 2D peaks of the particles produced at 250 and 1050 W (figure 8(b)) were similar to those reported for soot [32, 33] and were much broader than the sharp 2D peaks exhibited by the highly ordered graphene sheets produced under similar reactor conditions.
Figure 9. (a) A low-magnification TEM image of graphene sheets synthesized through the delivery of DME. Scale bar: 100 nm. (b, c) A high-magnification TEM image and the corresponding EELS spectrum of DME-synthesized graphene. Scale bar: 2 nm.

Figure 10. Low-magnification TEM images of graphene created through the delivery of ethanol at a plasma gas flow of 3.4 lpm and MFPs of (a) 250 W, (b) 650 W and (c) 1050 W. Scale bars: 100 nm.

3.4. Delivery of dimethyl ether

The materials synthesized through the delivery of DME resembled the graphene created from ethanol. The low-magnification TEM image shown in figure 9(a) reveals that transparent sheets hundreds of nm in size were produced. The sheets were typically folded, scrolled or overlapping, and exhibited homogeneous and featureless regions. A high-magnification TEM image of a graphene sheet is shown in figure 9(b). An EELS spectrum corresponding to the high-magnification image exhibited the 1s-π* peak at 285 eV and the 1s-σ* peak at 291 eV (figure 9(c)).

3.5. Delivery of ethanol at lower plasma gas flow rates

Graphene was synthesized at a plasma gas flow rate of 6.8 lpm. A reduction in the plasma gas flow rate to 3.4 lpm also resulted in the synthesis of atomically thin sheets. Low-magnification TEM images revealed that folded and overlapping sheets were created at every MFP setting investigated. Graphene synthesized at 250, 650 and 1050 W is shown in figure 10.
Graphene monolayers were observed at higher magnifications (figure 11), and the sheets exhibited single dark fringes characteristic of graphene. The corresponding EELS spectra for each of the high-magnification images exhibited sharp $1s$-$\pi^*$ and $1s$-$\sigma^*$ peaks at 285 and 291 eV, respectively (figure 11).
A reduction in the plasma gas flow rate to 1.7 lpm resulted in the formation of graphitic structures along with graphene sheets at every MFP setting tested. Dark particles were observed among the sheets in low-magnification TEM images (figure 12). Some particles had diameters of a few tens of nm, whereas others were hundreds of nm in size.

Intermediate-magnification images revealed that the graphitic particles consisted of curved graphene layers (figure 13). These particles were similar to graphitic particles that have been produced by arc discharge [34]–[37], vacuum deposition [38], ball-milling of graphite [39, 40], electron irradiation of soot [41] and heat treatment of carbon blacks [42, 43]. Particles with sizes greater than 100 nm were found to be bulk graphite structures consisting of hundreds of graphene layers (figure 13). These larger particles were similar to structures created in Ar/H$_2$/CH$_4$ microwave discharges [44].

High-magnification images and EELS spectra of graphene sheets, graphitic particles and bulk graphite structures were also acquired. The materials synthesized at 250, 650 and 1050 W are shown in figures 14, 15 and 16, respectively. Similar structures were produced and observed at every MFP setting investigated. EELS spectra obtained from the synthesized materials exhibited the 1s-$\pi^*$ and 1s-$\sigma^*$ peaks of graphite at 285 and 291 eV, respectively.

4. Discussion

4.1. The effect of precursor composition

The atomic composition of the precursors delivered into the argon plasmas had a significant effect on the materials produced in the reactor. Furthermore, the formation of soot particles from IPA offers a clue to a possible mechanism for the substrate-free gas-phase synthesis of graphene.

The formation of soot has been the subject of a large amount of experimental and computational research for decades. See [22] and references cited therein for details. Briefly, the prevailing theory is that individual soot particles are formed from polycyclic aromatic hydrocarbon (PAH). In both oxidative and non-oxidative environments, PAHs are formed from reactive species such as acetylene (C$_2$H$_2$), propargyl (C$_3$H$_3$) and H. Individual PAHs then experience abstraction by H atoms, and grow through the addition of acetylene molecules. Once formed, PAHs collide and stick to each other to form PAH dimers. The collision of PAH dimers with other PAHs then results in the formation of PAH trimers, PAH tetramers and so on. As these collisions occur, individual PAH molecules within these clusters grow via chemical reactions at their edges. These processes continue until PAH clusters evolve into individual soot particles.

The continued growth of soot particles has been theorized to occur via particle surface reactions. The surfaces of soot particles can be envisioned as being similar to the edges of large PAHs terminated with C–H bonds. The surfaces therefore also experience abstraction and growth through H and acetylene, respectively. Once spherical soot particles are formed, they collide and coalesce to form larger spherical particles. At the later stages of the process, larger particles collide with other particles and agglomerate into chain-like structures.

The carbonaceous particles produced from IPA in the present study (figures 6 and 7) strongly resemble the soot particles widely reported in the literature [23]–[27]. This implies that the mechanism for the synthesis of solid carbon materials in the microwave gas-phase process may be similar to the mechanism of soot formation. Indeed, reactive species, such as acetylene, propargyl and H, are readily produced through the dissociation of hydrocarbons in plasmas.
Figure 12. Low-magnification TEM images of graphene sheets, graphitic particles and bulk graphite structures synthesized at a plasma gas flow rate of 1.7 lpm and MFPs of (a, b) 250 W, (c, d) 650 W and (e, f) 1050 W. Scale bars: 100 nm.
Figure 13. Intermediate-magnification TEM images of graphitic particles and bulk graphite structures synthesized at a plasma gas flow rate of 1.7 lpm and MFPs of (a, b) 250 W, (c, d) 650 W and (e, f) 1050 W. Scale bars: 10 nm.
Figure 14. High-magnification TEM images and corresponding EELS spectra of (a, b) a bi-layer graphene sheet, (c, d) a graphitic particle and (e, f) a bulk graphite structure synthesized at 250 W and a plasma gas flow rate of 1.7 lpm. Scale bars: 2 nm.

These species can form PAHs, which in turn may form carbonaceous clusters and soot particles. The individual particles experience surface growth, coagulation and aggregation, resulting in the chain-like structures shown in figure 6.

If the dissociation of IPA resulted in the formation of soot, then how was graphene formed from ethanol? The results from the methanol experiments offer an additional clue to a possible
reaction mechanism. Methanol consists of a single C atom, whereas ethanol and IPA both contain multiple C atoms and C–C bonds. Relative to ethanol and IPA, the formation of a C–C bond through the dissociation of methanol and combination of the produced CH$_x$ fragments is much more of a challenge. The formation of a lower number of C–C bonds implies that less
Figure 16. High-magnification TEM images and corresponding EELS spectra of (a, b) a bi-layer graphene sheet, (c, d) a graphitic particle and (e, f) a bulk graphite structure synthesized at 1050 W and a plasma gas flow rate of 1.7 lpm. Scale bars: 2 nm.

Acetylene and propargyl are created. In turn, the smaller number of acetylene and propargyl molecules results in a decreased number of aromatic species. Furthermore, the growth of the aromatic rings in size is also hindered by the limited amount of acetylene available. Under such conditions, one should expect the formation of graphene sheets or other carbonaceous materials to be suppressed.

New Journal of Physics 12 (2010) 125013 (http://www.njp.org/)
The observed sooting tendencies of alcohols further support this argument. The ease of forming a C–C bond has long been argued to be the underlying cause of sooting tendencies in the combustion of fuels \[45, 46\]. The extent of soot formation for alcohols increases as the number of carbon atoms in the molecule increases \[46\]. For example, flames from secondary alcohols, such as IPA, have been found to be much ‘sootier’ than flames from primary alcohols, such as ethanol and methanol \[46\].

The presence of O atoms in alcohols may also affect the structures of the synthesized materials. Elemental analysis of microwave-synthesized materials has shown that the graphene sheets produced through the delivery of ethanol are free of oxygen \[14\], thus suggesting that the ethanol O atoms must be breaking from the C atoms, probably ending up in CO, during the synthesis process. Methanol consists of a single C atom and a single O atom, and the formation of C–C bonds may compete with the formation of C–O bonds. CO is relatively unreactive, and its formation in the non-oxidative environment of the reactor may have captured most of the C atoms present, thus preventing the formation of C–C bonds and aromatic rings. The production of CO has been shown to occur in low-pressure microwave plasma reactors when the precursor C/O atomic ratio was unity \[47\], and we suggest that this may also have occurred in the present methanol experiments. In contrast to methanol, ethanol and IPA each contain a single O atom per multiple C atoms. Thus, even if each O atom ties up a C atom in CO, more C atoms are available to form C–C bonds.

Based on these considerations, the substrate-free gas-phase synthesis of graphene through the delivery of ethanol may be thought of, in simple terms, as a ‘goldilocks condition’. The delivery of methanol may have yielded ‘too few’ C atoms to form C–C bonds, thus preventing the nucleation of a sufficiently large number of aromatic species and their growth into carbon structures. The dissociation of IPA may have yielded ‘too many’ C atoms, and thus an overabundance of PAHs formed and experienced multiple collisions with other PAHs to form clusters. These clusters then experienced growth, coagulation and aggregation to form chains of soot particles. The formation of graphene from ethanol perhaps indicates that the number of C atoms present in the reactor was ‘just right’. The creation of a sufficient number of C–C bonds may have resulted in the nucleation of an adequate number of initial aromatic species. A graphene sheet could be thought of as an extremely large PAH molecule. Therefore, it could be speculated that the synthesis of graphene was the result of a slow nucleation forming a small number of initial aromatic rings followed by their fast growth into large 2D sheets.

The synthesis of graphene from DME supports the argument that ethanol contained an ideal number of C, H and O atoms for the formation of graphene. The results of the DME experiments also showed that graphene was produced at a specific C/H atomic ratio. DME, ethanol, methanol and IPA all contain a single O atom. Graphene was created through the delivery of ethanol and DME (C/H = 0.333). Graphene was not produced through the delivery of methanol (C/H = 0.250) and IPA (C/H = 0.375). Thus, a range of precursor C/H ratios resulting in graphene synthesis may exist between the ratios of methanol and IPA.

### 4.2. The effect of microwave forward power

The synthesis of graphene was initially speculated to occur in the coupler region. With this assumption, increases in the MFP were expected to significantly affect the synthesis environment and affect the types of carbon structures produced in the reactor. However, we
observed that increasing the MFP did not affect the structures of the synthesized materials, regardless of the precursor composition. This indicates that the formation and growth of graphitic materials occurred in the plasma afterglow, an area of the plasma that extends above the coupler region.

The characteristics of the afterglows of atmospheric-pressure microwave-generated plasmas have been extensively studied [48]. Neutral gas temperatures in afterglows were found to be only slightly affected by increases in MFP. The average afterglow gas temperature was shown to increase from 3000 to 3400 K when the MFP was increased from 350 to 1100 W [48]. By correlating the similarity of the structures produced at every MFP to the similar afterglow environments generated at every MFP, it could be speculated that the primary role of the coupler region of the plasma during the synthesis process was the dissociation of alcohols. The reactive fragments created through the dissociation of alcohols then flowed out of the coupler region and underwent gas-phase reactions to form graphitic structures in the gases of the afterglow.

In addition to dissociating precursors, the microwave-generated plasmas may have played another destructive role during the synthesis process. Increasing the MFP has been shown to significantly raise the electron temperature in the reactor [48]. Although electron densities are only slightly affected by changes in MFP [48], the fraction of electrons with energies capable of ionization and dissociation does increase with MFP. It could therefore be argued that a larger number of reactive species were created in the coupler region because of a larger population of energetic electrons. The increased collisions between larger numbers of reactive species in the afterglow should then have resulted in a faster formation of PAH species and, consequently, in the growth of soot-like carbonaceous particles instead of graphene sheets. However, the ethanol experiments showed that this assumption could not be entirely correct, since graphene was synthesized at every MFP setting. Taken together, these observations suggest that reactive fragments were not only being created in the coupler region but may have also been destroyed by the energetic electrons at elevated MFPs. The production of reactive fragments could have increased with the MFP, which resulted in the increased yield of solid materials at higher MFPs. However, the destruction of reactive species may have also increased with MFP, which could have retarded the formation of carbonaceous clusters and soot particles.

4.3. The effect of plasma gas flow rate

Graphitic particles and bulk graphite structures were produced along with graphene sheets through the delivery of ethanol at the lowest plasma gas flow rate investigated. These results suggest that the decreased flow rates provided enough time for aromatics to form, rapidly grow into individual graphene sheets and stack into ordered graphite structures. The stacking of graphene may explain the production of sheets and particles consisting of tens to hundreds of layers. However, the formation of curved graphitic particles showed that other processes may have also taken place during the prolonged residence time. Graphitic particles have been reported in the literature, and the materials have been created through various methods [33–43]. Numerous mechanisms have been proposed for the formation of these particles, and one or more of these mechanisms may have occurred in the reactor at lower plasma gas flow rates.

The synthesis of graphitic particles in the reactor could have been a result of the formation of multi-layered graphite sheets. The edges of some of the sheets may have contained dangling bonds instead of being terminated with H atoms, which could have been caused by H abstraction.
or electron impact. The curving and closure of a graphite sheet into a graphitic particle could have taken place when the edges of the sheet joined to eliminate these dangling bonds, thus attaining a minimization of free energy. This mechanism has been used to explain the curving and closure of graphite sheets that have been produced through the ball-milling of graphite [39, 40]. Ball-milling could be thought of as a top-down approach of obtaining graphitic particles, while microwave gas-phase synthesis could be envisioned as a bottom-up technique. Although the two methods are completely different, the mechanism for the formation of graphitic particles may have been similar.

Another possible mechanism for graphene sheet curvature is through the formation of pentagonal rings at graphene edges [49]. The extent of curvature in this case will be governed by competition between the formation and destruction of five-member rings, which in turn will be controlled by the plasma energy and hence by MFP.

The formation of graphitic structures from graphite sheets raises an interesting question: if these three-dimensional (3D) sheets curl and close to minimize the free energy, then how could 2D synthesized graphene sheets exist? Firstly, some of the multi-layer sheets did not form graphitic particles. Free-standing sheets consisting of ten or more graphene layers were observed among the synthesized materials. Secondly, elemental analysis revealed that the graphene sheets were composed of 1% H by mass [14]. These H atoms may have been located at the edges of the graphene sheets, thus terminating dangling bonds and preventing closure. Thirdly, free-standing graphene can exist even without H atoms at the edges. HOPG is a pure carbon material, and the creation of single-layer graphene through the mechanical exfoliation of HOPG initially puzzled researchers. It was argued that the sheets existed because they were derived from 3D crystals [1]. The substrate-free microwave synthesis of graphene disproved that theory. Another argument for the existence of graphene is that the monolayer sheets become intrinsically stable by gentle crumpling in the third dimension [1, 16]. These corrugations increase the elastic energy in a sheet but minimize thermal vibrations, which lowers the free energy at room temperature [1, 16]. Thus, the synthesized graphene sheets can exist in a free-standing state, regardless of the presence of H atoms at the edges, because of gentle 3D warping.

Another pathway to the formation of graphitic particles in the reactor could be similar to the mechanism proposed in arc-discharge synthesis experiments [35]–[37], [50]. Polyhedral graphitic particles produced by arc discharge have been speculated to originate from carbonaceous clusters that form due to the condensation of carbon vapor in inert gas atmospheres [35]–[37], [50]. These clusters resemble individual spherical soot particles [36, 37]. The clusters grow into larger particles via coagulation and maintain a ‘structural fluidity’ due to the high temperatures (3500 K) and the bombardment of ions and electrons in the arc discharge [37]. Because of this structural fluidity, the particles have been referred to as ‘liquid carbon droplets’ [36]. Graphitization of the liquid carbon droplets occurs during cooling, which proceeds from the surface of the particles to the center [36, 37]. Graphite planes are initiated at the outer surface of a particle, and internal planes form and remain parallel to the outer layers as the particle cools [36, 37]. The flat planes of the shells consist of hexagonal rings, and the corners of the particles are a result of pentagonal rings. This graphitization process results in polyhedral graphite particles with hollow centers, which form because the density of graphitized carbon (2.2 g cm$^{-3}$) is higher than that of amorphous carbon (1.5 g cm$^{-3}$) [36, 37]. The resulting structure minimizes dangling bonds and lowers the energy of the graphite particle [37].
Similar conditions for the formation of graphitic particles in arc-discharge processes were achieved in the present reactor. Gas temperatures in the afterglow have been measured to be in excess of 3000 K [48], and energetic ions and electrons were present in the region. As evidenced by the soot particles synthesized in the IPA experiments, carbonaceous clusters could be formed in the reactor. At lower flow rates and increased residence times, the aromatic nuclei created through the dissociation of ethanol could have experienced an increased number of collisions with other aromatics. These collisions could then have resulted in the formation of carbonaceous clusters, which then experienced growth by coagulation and surface reactions. However, in contrast to the aggregates of particles formed from IPA, the population of these clusters may have been low enough that the resulting particles grew without agglomeration. The particles could have achieved a structural fluidity in the afterglow due to the high temperatures and bombardment of charged species. Rapid cooling in the post-plasma regions of the torch could then have resulted in the graphitization of these ‘liquid carbon droplets’.

The high gas temperatures and energetic electrons in the afterglow may have also played a different role in the formation of graphitic particles at increased residence times. Annealing disordered soot particles at 2623 K has been shown to result in their transformation into graphitic particles [33, 42, 43]. Intense electron bombardment has also transformed soot into onion-like carbon particles consisting of concentric graphite shells [41]. It was theorized that electrons can cause ‘knock on’ damage, displacing carbon atoms to different sites, thus creating ordered hexagonal networks and pentagonal rings [41]. The formation of pentagonal rings in a hexagonal network of carbon atoms results in curved graphitic structures such as fullerenes [51], the end caps of nanotubes [37, 52], polyhedral graphitic particles [35] and curved graphene sheets [49]. While it could be theorized that annealing in gas temperatures over 3000 K and irradiation by energetic electrons were the primary mechanisms for the synthesis of graphitic particles, this argument is highly unlikely. Graphitization by annealing and electron bombardment requires time scales of the order of minutes to hours, which is a much longer period of time than the residence times of precursors in the reactor. Additionally, ‘irradiation-stimulated graphitization’ required a focused electron beam generated by a 300 kV TEM [41], which is a phenomenon that is impossible to create in the reactor. Therefore, instead of being the mechanisms for the formation of graphitic particles, the high temperatures and energetic electrons in the reactor may have facilitated the other mechanisms discussed above.

5. Conclusions

The results of experiments conducted in different experimental conditions and precursor compositions have provided substantial insight into the substrate-free gas-phase synthesis of graphene. Graphene synthesis was significantly affected by precursor composition and plasma gas flow rate. These parameters directly influenced the nucleation, growth and residence time of the materials produced in the reactor.

The production of soot from IPA, no solid structures from methanol and graphene from ethanol and DME showed that the challenge in the formation of C–C bonds dictated the structures produced in the reactor. The results of these experiments suggested that initial aromatic nuclei formed slowly, but the growth of these species was extremely fast. The synthesis of graphene from ethanol may therefore have been a result of the rapid growth of a small number of aromatic nuclei, while the production of soot from IPA could have been caused by the formation of a larger number of aromatics, which collided with each other to form
carbonaceous clusters and subsequently aggregates of soot particles. Based on these findings, ethanol and DME could have the ideal ratio of C, H and O atoms for graphene synthesis. It could therefore be argued that graphene could be produced by sending other organic and non-organic compounds into plasmas. For instance, graphene sheets could be synthesized through the delivery of other alcohols, mixtures of various alcohols, oxygenated hydrocarbons and their mixtures, non-alcoholic substances, mixtures of oxygenated and non-oxygenated compounds, as well as other gaseous and solid organic compounds. The results also indicate that precursors to the formation of aromatic nuclei, such as acetylene and benzene, could be sent into the reactor to obtain graphene. Additionally, graphene could be created through the delivery of PAHs into plasmas, such as naphthalene (C<sub>10</sub>H<sub>8</sub>), pyrene (C<sub>16</sub>H<sub>10</sub>) and coronene (C<sub>24</sub>H<sub>12</sub>). These PAHs could be mixed with other compounds, both organic and non-organic, to synthesize graphene sheets.

The plasma gas flow rate also had an effect on the structures produced in the reactor. Decreasing the plasma gas flow rate resulted in the production of graphitic structures along with graphene sheets. 3D graphite sheets and large bulk graphite structures were believed to have been formed from the growth, collision and stacking of individual graphene layers during the prolonged residence time in the reactor. The formation of graphitic particles could have been a result of the curving and closure of graphite sheets to eliminate dangling bonds or the graphitization of ‘liquid-like’ carbonaceous clusters. It could therefore be speculated that decreased residence times during the decomposition of IPA could prevent the formation of carbonaceous clusters, while increased residence times during methanol dissociation could allow for PAHs to form and grow into graphene monolayers.

Increasing the MFP did not affect the structures of the synthesized materials, and the production of graphene at low MFPs identified easier routes for graphene synthesis. It could be argued that graphene could be produced by sending any of the precursors mentioned above into low-power plasmas generated using either microwave or other energy-assisted reactors, such as radio frequency, dc, thermal or a combination of them. Furthermore, the substrate-free gas-phase synthesis of graphene could be achieved through non-argon plasmas or through thermal routes, such as thermal CVD, heating, pyrolysis or flame synthesis.

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