Graphene Synthesized in the Gas Phase: Research and Applications

A. Dato*

*Harvey Mudd College, Claremont, CA, USA, adato@hmc.edu

ABSTRACT

Pure and highly ordered graphene can be rapidly and continuously produced through the substrate-free gas-phase synthesis method. The single-step process involves sending precursors, such as ethanol and dimethyl ether, directly into atmospheric-pressure microwave-generated argon plasmas, which results in the formation of high-quality graphene. The most recent research into gas-phase-synthesized graphene will be presented. Factors affecting the production of graphene, such as gases, precursors, and precursor delivery methods, will be reported. Furthermore, the performance of gas-phase-synthesized graphene in a number of applications will be discussed. The experimental results elucidate the complex processes occurring in the bottom-up production method and demonstrate feasible applications for graphene synthesized in the gas phase.

Keywords: graphene, nanocomposite, composite, tribological applications, 2D materials

1 INTRODUCTION

Graphene is a remarkable two-dimensional material that posseses unique mechanical, thermal, and electrical properties. As a result, graphene sheets have been envisioned for use in numerous applications. The large-scale production of pure and highly-ordered graphene is needed for the realization of these applications. High-quality graphene can be produced through the gas-phase synthesis method, which involves sending an aerosol consisting of argon gas and liquid ethanol droplets directly into atmospheric-pressure microwave-generated argon plasmas. This paper will review research into the substrate-free production process and discuss the potential applications of gas-phase-synthesized graphene.

2 GAS PHASE SYNTHESIS METHOD

An atmospheric-pressure microwave (2.45 GHz) plasma reactor (MKS/ASTeX AX2518) was used to synthesize carbon nanomaterials in the gas phase [1-3]. A schematic of the reactor is shown in Figure 1. Argon plasmas were generated by passing argon gas through a quartz tube (21 mm internal diameter). The tube passed through a microwave guide, and plasmas were generated at an applied microwave forward power of 250 W. Aerosols consisting of argon gas and precursor droplets were sent through a smaller alumina tube (3 mm internal diameter). The alumina tube terminated directly below the coupler region, which was the central region of the reactor where electrons in the ionized plasma gas coupled with the applied microwaves. The alumina tube delivered aerosols directly into the plasmas. Precursors dissociated in the plasma to form solid matter, which were then collected downstream on nylon membrane filters.

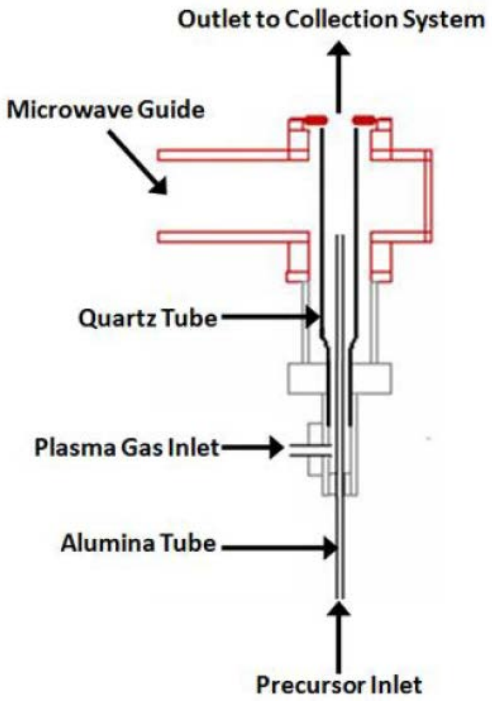

Figure 1: Schematic of the atmospheric-pressure microwave plasma torch. Adapted from reference [3].

3 SYNTHESIS OF NANOMATERIALS

3.1 Graphene Synthesis from Ethanol

Graphene sheets were produced by sending aerosols consisting of argon gas and liquid ethanol (C_2H_6O) droplets into atmospheric-pressure argon plasmas. Figure 2 shows a transmission electron microscopy (TEM) image of gas-phase-synthesized graphene, which reveals that they are crumpled and randomly oriented. Raman spectroscopy confirmed that the nanomaterials produced in the plasma reactor consisted of graphene. The D and G peaks positioned at 1350 and 1580 cm^{-1}, respectively, can be seen in Figure 3. Furthermore, the synthesized sheets exhibited a single, symmetric 2D peak below 2700 cm^{-1} that is characteristic of graphene. Elemental analysis has revealed

that the synthesized sheets have a composition of 98.9% C, 1.0% H, and 0.0% N (0.1% O by difference) [2], which shows that oxygen from the ethanol does not bond to the graphene during the synthesis process.

A very recent study has revealed that gas-phase-synthesized graphene does not behave like folded paper, but rather exhibits a significantly different behavior. In-situ TEM has revealed that the synthesized sheets contain graphitic staples that maintain the material's crumpled morphology and enable graphene to reversibly deform without strain hardening [4]. These graphitic staples are local regions of graphite that impart substantial additional mechanical stability and prevent crumpled graphene from being flattened like paper.

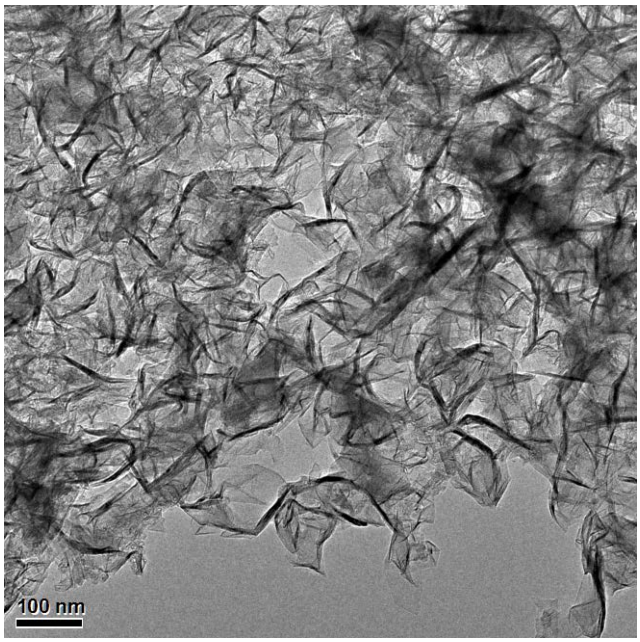

Figure 2: Gas-phase-synthesized graphene produced from ethanol. Scale bar is 100 nm.

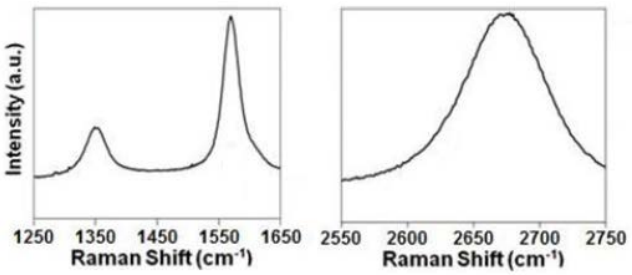

Figure 3: Raman spectrum of graphene synthesized in the gas phase.

Atomic-resolution imaging revealed that the synthesized graphene sheets are highly ordered [2]. Individual carbon atoms appear white and are arranged in a hexagonal pattern in the TEM image shown in Figure 4.

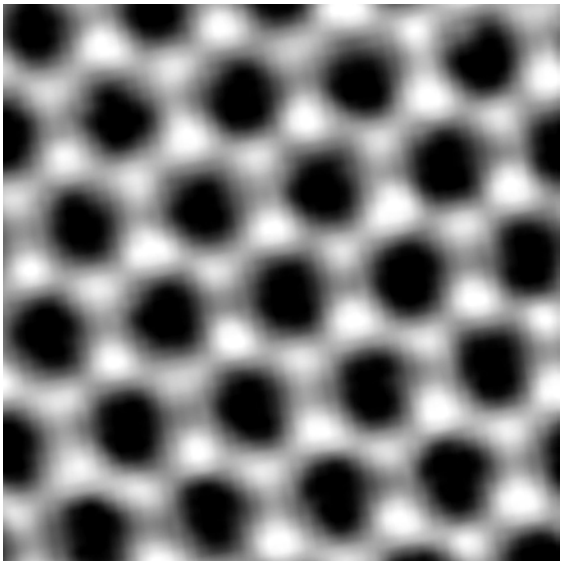

Figure 4: An atomic-resolution image of a clean and structurally perfect gas-phase-synthesized graphene sheet. Individual carbon atoms appear white in the image. The image was obtained through the reconstruction of the electron exit wave function from 15 lattice images using MacTempas software. Adapted from reference [2].

3.2 The Effect of Microwave Power

Increasing the applied microwave forward power has been shown to have no effect on the nanomaterials produced in the plasma reactor, which indicates that the formation and growth of graphene occurs in the plasma afterglow, an area of the plasma that extends above the coupler region [3]. Graphene was produced at applied microwave forward powers as high as 1250 W.

3.3 The Effect of Plasma Gas Flow Rate

The flow rate of the argon gas used to generate plasmas has a significant effect on the nanomaterials produced in the reactor. Decreasing the plasma gas flow rate increases the residence time of reactive species in the region of the plasma where nucleation and growth of carbon nanomaterials occurs. As a result, graphitic structures along with graphene sheets have been produced at lower plasma gas flow rates [3].

3.4 The Effect of Precursor Composition

The atomic composition of the precursors delivered into microwave-generated argon plasmas had a significant effect on the synthesized materials. Solid matter was not produced when aerosols consisting of liquid methanol (CH_4O) droplets and argon gas were sent into the plasma reactor. As shown in Figure 5, soot particles were obtained through the delivery of argon and propyl alcohol (C_3H_8O) droplets. The peaks in the Raman spectrum shown in Figure 6 indicated that soot was indeed produced [3].

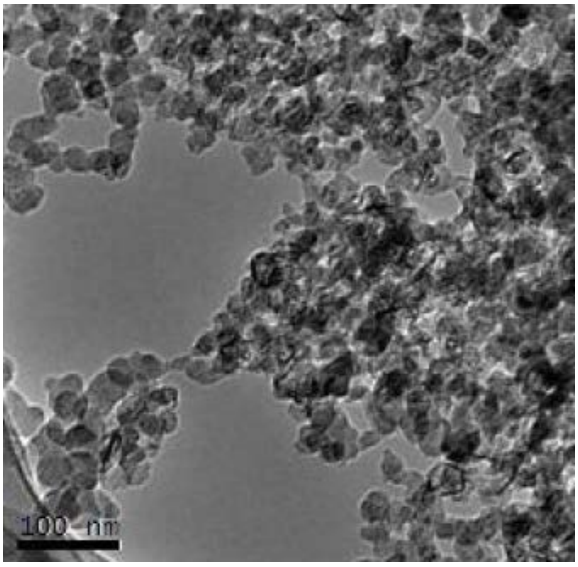

Figure 5: Soot particles produced from propyl alcohol. Scale bar is 100 nm.

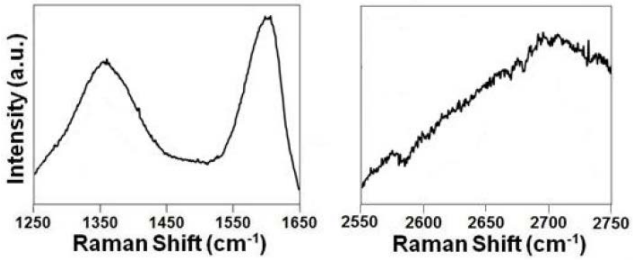

Figure 6: Raman spectrum of soot particles produced from propyl alcohol.

Interestingly, the injection of dimethyl ether (C_2H_6O) into the plasma reactor also resulted in the formation of the randomly oriented and crumpled graphene sheets shown in Figure 7 [3].

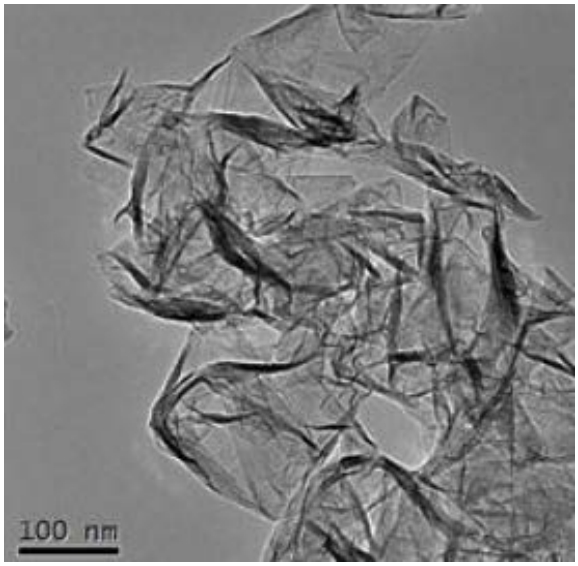

Figure 7: Graphene produced from dimethyl ether. Scale bar is 100 nm.

The synthesis of graphene from dimethyl ether indicates that ethanol contained an ideal number of C, H and O atoms for the formation of graphene. The results of the dimethyl ether experiments also showed that graphene was produced at a specific C/H atomic ratio. Dimethyl ether, ethanol, methanol and propyl alcohol all contain a single O atom. Graphene was created through the delivery of ethanol and dimethyl ether (C/H = 0.333). Graphene was not produced through the delivery of methanol (C/H = 0.250) and propyl alcohol (C/H = 0.375) [3]. Thus, a range of precursor C/H ratios resulting in graphene synthesis may exist between the ratios of methanol and propyl alcohol.

4 APPLICATIONS

The first application of gas-phase-synthesized graphene was an atomically thin TEM support film. As shown in Figure 8, the pure and highly ordered nature of the synthesized sheets enabled the atomic-resolution TEM imaging of the interfaces of gold nanoparticles and their soft citrate coatings for the first time [5].

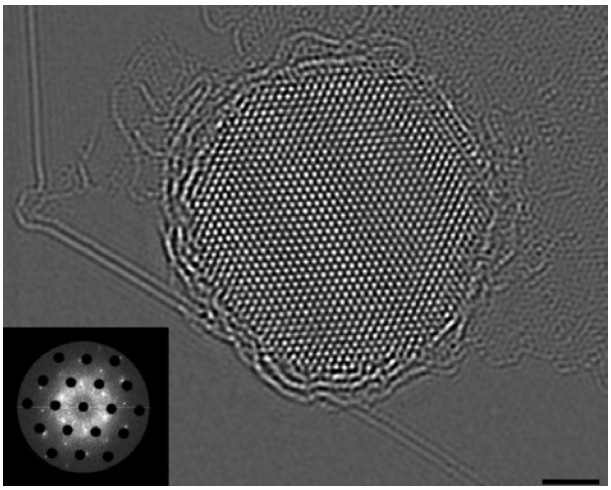
Figure 8: Graphene-enabled isolation and imaging of citrate molecules. An enhanced-contrast filtered image of the citrate-capped gold nanoparticle. (Inset) The graphene reflections were subtracted in a digital diffractogram of the entire image. Scale bar is 2 nm. Adapted from reference [5].

Gas-phase-synthesized graphene could potentially be used in the many applications that have been envisioned for graphene powders such as graphene oxide (GO), reduced graphene oxide (RGO), and graphene nanoplatelets (GnPs). These applications include multifunctional nanocomposites [6], water purification [7], energy storage [8], and electrically conductive inks [9]. Unlike GO, RGO, and GnPs, the production of GSG does not require the mining of flake graphite or the use of hazardous chemicals. Furthermore, the gas-phase synthesis process is scalable for industrial applications, and the ethanol and power required to generate plasmas can be produced from renewable resources.

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