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Progress in top-down production of graphene

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Abstract

In this review, the focus is on recent studies into production methods of graphene classified as "top-down". The methods are electrochemical exfoliation, liquid phase exfoliation (LPE), and liquid-phase pulsed laser ablation (LP-PLA). Each method is introduced and discussed based on changes that can be made to the chemistry involved, the layout and tools of the method, or additional steps taken. As graphene is looked at increasingly for research purpose, it is important to optimize its processing and gain a better understanding of each. TEM and SEM imagery help to give an indication of the structure, quality and morphology of graphene product made.

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1. Introduction

Graphene remains a novel, exciting material, and has found many uses. Part of the attention it has received is due to its amazing properties, such as a high Young's modulus, high carrier mobility, high thermal conductivity, and low light absorption [1].

Since its isolation, many methods have been devised to produce it beyond simple mechanical exfoliation. The top-down methods, which are related to mechanical exfoliation, have similar aspects which studies investigate. Most of the studies reported on revolve around making graphene that is low in impurities, has a fewer number of layers, and is produced in high yields. Through altering the chemistry or layout of the method, improvements have been made. Changing the steps taken in "post-processing", the procedure taken after the main process, also has an impact on the graphene product made. Many of the studies are guided by an attempt to refine and scale up each technique to get it to a level capable of industrial production. Regardless of whether the improvements ever impact industrial scale-up, they show the possibilities of making better graphene. Since the properties and physics behind graphene are still an active area of research, top-down methods such as Liquid-Phase Pulsed Laser Ablation (LP-PLA) [2] can be used to make graphene that is suitable for these studies; it is a possible improvement from the graphene which is prepared by peeling exfoliating strips of graphene away from graphite [3]. As well, the investigation of each step helps to provide an understanding of the technique used.

1.1. Structure

Graphene in its single-layer form has a two-dimensional hexagonal surface in which every electron orbital is sp^2 hybridized with three covalent bonds to adjacent carbon atoms and a free electron resting in the p_z orbital above the atomic plane, where it forms a π bond with adjacent free electrons [4]. This form has carbon-carbon double covalent bonds alternating with carbon-carbon single covalent bonds in each hexagon of the surface. Graphite, from which graphene is derived, has a multilayered hexagonal structure with Van der Waals bonds connecting each layer of graphene [5].

Traditional exfoliation methods of making mono-layer graphene involve a break of the Van der Waals bonds leaving only the carbon-carbon covalent bonds, the strongest of all chemical bonds, on a single layer. Few-layer graphene (**Fig. 1**), or a graphene nanosheet several atomic layers thick, is another structure that can be made by processing graphene. The studies considered here involve optimized processes for the creation of few-layer graphene, which is taken to be under ten layers thick.

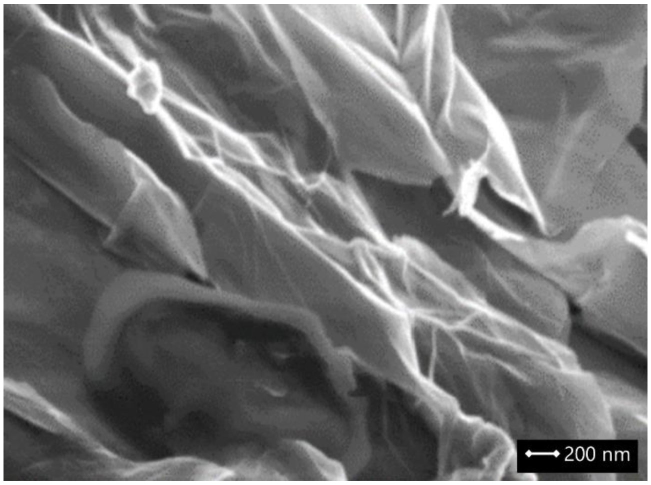

Figure 1. Field Electron-Scanning Electron Microscopy (FE-SEM) image of few-layer graphene prepared using Liquid Phase Exfoliation that tested different ratios of acid in the liquid used. This image shows layers and folds in the graphene made through this top-down method. Modified image from [1].

2. Top-Down Production Methods

The two classes of production methods that exist for graphene are top-down and bottom-up. Top-down methods exfoliate graphene from the stacked structure of multiple layers into a single layer or several layers of graphene, through mechanical or other means [6]. Simplified mechanical exfoliation is often used for producing small quantities of graphene in research capacities, or through a "tear-and-stack" method used in conjunction with hexagonal boron nitride in physics investigations [3]. The bottom-up class produces graphene via deposition of a material, such as chemical vapor deposition, epitaxial growth, or arc discharge [7]. The focus here is on the study of three top-down methods, electrochemical exfoliation, liquid-phase exfoliation (LPE), and liquid-phase pulsed laser ablation (LP-PLA). All three involve processing a form of graphite in some liquid medium, but the appropriate liquid for one method is not necessarily the same as for the other.

2.1 Characterization

Each of the studies reported on used many of the same analysis and characterization methods, such as observing field emission scanning electron microscopy (FE-SEM) images and high-resolution transmission electron microscopy (HR-TEM) images to study the morphology and structure of the graphene made. SEM and TEM images are included in this article to provide the reader with an idea of the resolution of the graphene made using each of the three processing techniques described.

Raman spectroscopy was also used for further determination of the structure, quality, and amount of graphene produced. The spectra produced by this technique give the intensity of light scattered against the Raman shift, or energy difference between the incident and scattered light [6]. These intensities, the D, G, and 2D peaks have characteristic values for graphene of ~1360 cm^{-1}, ~1590 cm^{-1}, and ~2700 cm^{-1}, respectively [8]. The D peak is activated by defects within the structure, such as edge defects, structural disorder, and functional groups present [1, 6]. The G peak corresponds to the first-order scattering of the E_{2g} mode of sp_2 carbon atoms [6]. The 2D peak shape helps to identify the layers of graphene in the product [6]. The ratio of the intensity of the D band peak to that of the G band peak, I_D:I_G, is used to gauge the quality and the degree of defects within the graphene product [1, 9].

Beyond imaging and Raman spectroscopy, some studies utilized X-ray diffraction (XRD) [10] and energy dispersive x-ray spectroscopy (EDXS) to analyze samples. XRD is useful in recognizing defects present in graphene, as intensities are higher when defects are present [10].

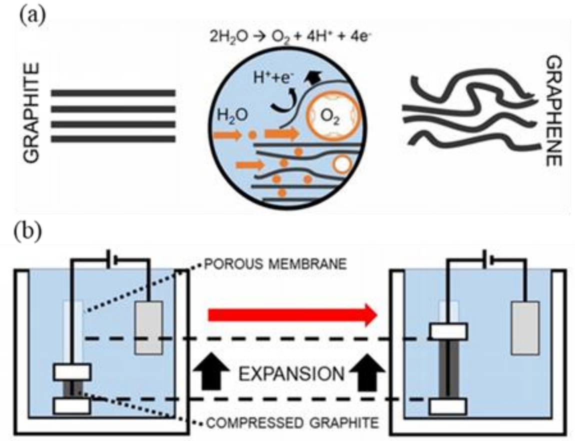

Figure 2. (a) Schematic of the electrochemical exfoliation process, showing the intercalation of electrolyte ions between graphite layers which expand and break Van der Waals forces holding together the material, leading to separated layers of graphene. **(b)** A modified version of an electrochemical cell using free graphite in a porous, expandable cathode to increase the amount of graphite utilized in the reaction. Adapted from [6].

3. Electrochemical Exfoliation

3.1 Process

The electrochemical method uses the charged ions of an electrolyte to intercalate between layers of a graphite electrode, which expand the material and allow individual layers of graphene to be separated. A schematic of this process is shown in **Figure 2(a)**. Either cathodic or anodic potential can drive the reaction [8]. The final product is treated in some additional step, such as centrifugal washing, placement in a water suspension, or vacuum filtration.

3.2 Studies of Electrochemical Exfoliation

Each of the three studies involving electrochemical exfoliation attempted to optimize the process in some manner. This search for improvements provides a better understanding of the mechanisms underlying electrochemical exfoliation and post-processing.

Each study chose a graphite-containing material for the working electrode and a good counter electrode. A study done by Mir et al. used highly oriented pyrolytic graphite as the cathode with a platinum electrode [11]. Ilias et al. used a graphite rod and a platinum plate [8]. The reactions were run to completion in each study, but in the study carried out by Achee et al., it was noted that past work involving graphite rods had unused material that collected at the bottom of the container, decreasing reaction efficiency [6]. The researchers of Achee et al. sought to solve this issue by instead using a permeable, expandable membrane containing graphite flakes as the cathode (**Fig. 2(b)**). Graphite flakes remained electrically connected to a graphite counter electrode by a wire, allowing for the exfoliation process to occur with more graphite used. After exfoliation and sedimentation occurred, the yield of graphene was 38% of the original weight of graphite. They increased yield to 65% of the original weight by modelling the cathode as an electrically conductive cylinder and redesigning it for an increased surface-to-volume ratio and forced-in electrolyte flow. With this redesign, the researchers found that reaction efficiency was unaffected as the electrode was made larger [6].

The same study done by Achee et al. used ammonium sulfate as the electrolyte for the reaction [6]. The other two studies used sulfuric acid [8, 11], however, Ilias et al. altered the acid concentration to understand what effect it had on the graphene produced. The electrolyte used was composed of 0.1 M sulfuric acid and 0.1 M potassium hydroxide, using volume ratios of 90:10, 80:20, and 70:30 sulfuric acid: potassium hydroxide [8]. The electrolyte with the highest acid concentration was the one which yielded the best product. The Raman spectra of analyzed samples showed the greatest number of layers and minimal number of defects for the highest concentration of acid (**Fig. 3**), quantized by the I_D:I_G ratio. FE-SEM images showed that higher acid concentration caused more layering and folding, (**Fig. 4(a)**), whereas lower acid concentration led to a more platelet appearance, like that of graphite (**Fig. 4(b)**). Energy dispersive X-ray spectroscopy results showed that the higher acid concentration graphene was also the least oxidized of the three electrolytes.

The study by Ilias et al. used an initial voltage of 2.5 V to expand the graphite and allow hydroxide ions in, then increased it to 10 V to actuate exfoliation of graphene [8]. Achee et al. kept the voltage at 10 V, reporting varied times for electrochemical expansion [6]. Mir et al. took additional steps in getting to the final product so that they ended up with a controlled number of layers and graphene flake size. They performed an investigation into a suitable current density for electrochemical exfoliation, power density for ultrasonication, structure has a weaker interaction between graphene layers, which made it easier for ultrasonic cleaving to generate flakes of tri-layered graphene, as was confirmed through TEM imaging and Raman spectroscopy [11].

The group started off at 100 mA/cm2 current density, finding that it was not sufficient to exfoliate larger flakes and resulted in smaller-sized flakes, while 300 mA/cm^2 caused too much agitation and broke apart larger flakes. 167 mA/cm^2, in the middle of the tested current densities, gave the largest average flake size. An increase in input power density during

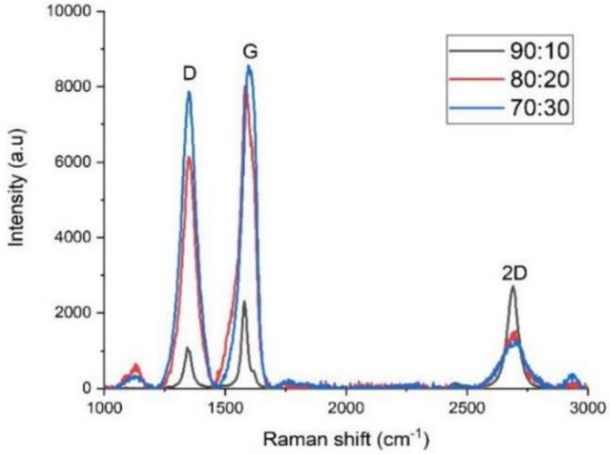

Figure 3. Raman spectrum for graphene prepared by electrochemical exfoliation using a sulfuric acid-potassium hydroxide electrolyte in ratios of 90:10, 80:20, and 70:30. The 90:10 ratio made for the lowest defect ratio out of the three. This ratio is found by comparing the D band intensity to the G band intensity (I_D:I_G). Image from [8].

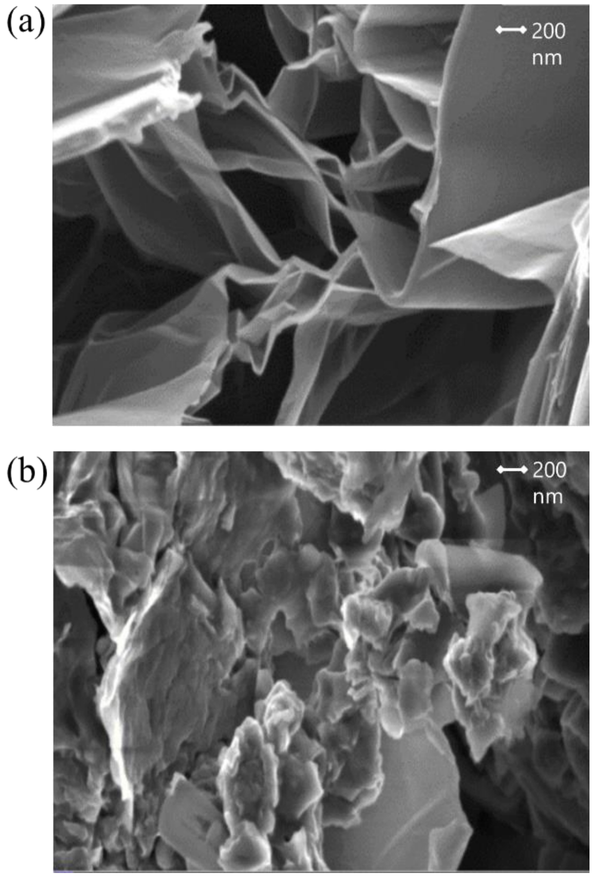

Figure 4. FE-SEM images showing graphene samples prepared by electrochemical exfoliation with a sulfuric acid-potassium hydroxide electrolyte in ratios of (a) 90:10, showing more sheet-like structures that are stacked, and (b) 70:30, showing clumped carbon structures, like that of graphite. Adapted from [8].

and speed for centrifugation. They first made an intermediate product, graphite bisulfate, which is tri-layered graphene separated by intercalant molecule planes of bisulfate. This ultrasonication yielded a larger number of graphene flakes that were entirely tri-layered, and it was found that 150 W/cm^2 was the optimal power density. When the group increased the centrifugation speed up to 2,000 rpm, the graphene flakes produced had the largest fraction of tri-layered graphene for all centrifugation speeds tested. Under the optimized conditions, the researchers reported that it was possible for them to make a tri layered suspension with an average flake area of around 20 μm^2 and an average tri layered graphene content of 90% with 40% of the flakes completely tri layered [11]. In contrast to the study by Mir et al., Ilias et al. did note that their samples all had average sheet diameters of 200 nm [8]. Through one post-treatment of their electrochemically-produced graphene, involving shear mixing, Achee et al. found that the lateral size was around 40 μm^2 [6].

Each of the three studies made a step in understanding the processing of graphene through electrochemical exfoliation: efficiency can be increased by changing the form of the electrode used [6]; the electrolyte used can affect the chemistry during the process, leading to a higher quality product [8]; the consistency of the product can be altered by changing the power and speeds used during and after electrochemical exfoliation [11].

4. Liquid Phase Exfoliation

4.1 Process

The process for LPE involves placing a dispersion of graphite in liquid media which helps to separate weakly-held graphite layers. The rest of the process is actuated through either sonication or shear mixing to further separate graphene from graphite [4, 12]. A more detailed look into the process was done in a study by Li et al. [13], using fewer solvent choices to understand the change of surface chemistry in graphite as the process occurred. They identified three distinct stages to the process. The first stage involves the rupture of flakes via sonication, leading to complex damage of graphite flakes from slip of a basal plane and the formation of high-strain, chemically active kink bands that have twin boundaries. In the second stage, the kink bands become oxidated from species in the solvent and fracture apart, allowing for the peeling of thin graphite strips. The third stage involves more fragmentation, and exfoliation to end up with a product of few-layer graphene flakes [13].

4.2 Studies of Liquid Phase Exfoliation

One downside to LPE is that the process can be inefficient, leading to a low yield of graphene [13]. The studies included here investigated the effects of modifying the liquid used on the efficiency of the process [4, 12], while one also looked into the sonication step for optimization [4].

Güler et al. tested six organic liquids, finding the three most efficient to be 2-propanol with sodium dodecyl sulphate (SDS), ethanol with SDS, and N-Methyl-2-Pyrrolidone (NMP) [4]. The SDS was used as a surfactant to decrease the surface tension of the former two liquids to the level required to break apart Van der Waals forces holding together the graphite, thereby increasing yield. The NMP proved to be efficient without any modifications.

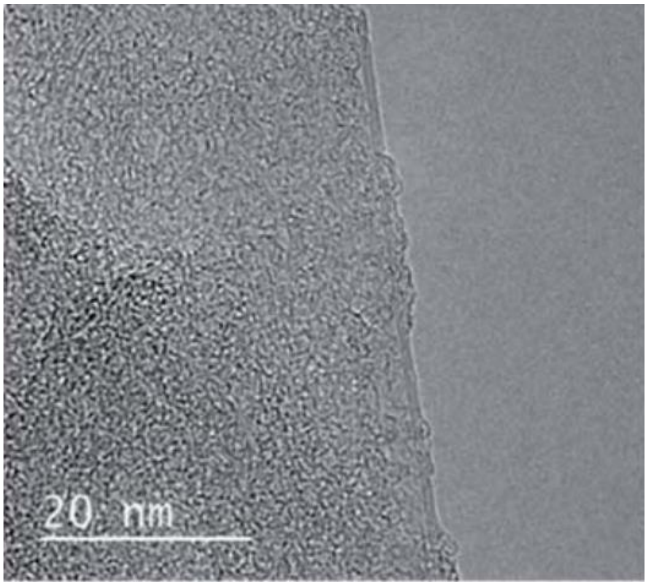

Figure 5. High-Resolution TEM image of a three-layer thick graphene flake prepared by liquid phase exfoliation in water modified with a bis-pyrene stabilizer at a 0.6 mg/mL concentration. This study demonstrated the efficiency of the stabilizer in exfoliating graphite and creating thin layers. Modified image from [12].

The graphene suspensions produced using these liquids were stable for the longest amount of time before experiencing sedimentation of produced graphene [4]. Because of this longer stability, the suspensions yielded more graphene. These liquids also gave the thinnest and most transparent graphene layers out of all suspensions looked at.

The study by Shin et al. used water with water-insoluble bis-pyrene stabilizers (BPS) to enhance interaction strength with graphite by two pyrene groups [12]. The stabilizer used in the study was formulated by using a pyrrolidine central group as the functional group. This proved to be very efficient at exfoliating graphene away from graphite, much like the NMP used in the study by Güler, which also has a pyrrolidine group in its structure. As the concentration of bis-pyrene stabilizers was increased, the graphene concentration in the dispersions made was higher; the higher concentration of the stabilizer made the process more efficient, owing to its good adsorption onto graphene. An HR-TEM analysis performed for graphene that was prepared using 0.6 mg/mL concentration of BPS in water gave evidence of successful exfoliation from graphite. The sample was composed of three layers, seen in **Figure 5**.

Beyond choosing a good liquid medium, the sonication step can also play a role in the amount of graphene made. Güler et al. investigated the optimal power and time for the sonication process before investigating the effects of different liquids [4]. Using only dimethylformamide for the liquid medium, they used a sonication power of 375 W , 50% of the maximum power used, for 4 hours, their longest sonication time they tested. The researchers found that the optimized parameters for sonication gave them the most graphene and the lowest degree of defects, using the 2D peak intensity and the I_D:I_G ratio of Raman spectroscopy, respectively. TEM imagery showed that optimized sonication led to the thinnest and most transparent of all graphene which they made.

In the two studies, liquids were chosen and modified to improve their interaction with graphite and make the process of graphene exfoliation from graphite more efficient. Optimizing the step that actuates exfoliation can further help to make an efficient process.

5. Liquid-Phase Pulsed Laser Ablation

5.1 Process

A newer top-down method, LP-PLA, uses a laser to break down the structure of a graphite-containing target material within a liquid medium capable of breaking graphene off from the graphite. A laser beam increases the temperature of the irradiated spot, vaporizing the target and resulting in collisions between evaporated species and the surrounding molecules of the liquid [14]. Excited electrons combine with generated ions and electrons to form a region of plasma above the target surface, termed a plasma "plume". At the edge of this plume, nanoparticles are formed through supersaturated vapor nucleation, experiencing a massive temperature decrease.

The process is outlined in Fig. 6(a) and has been used for generation of nanoparticles from other materials, as well as graphene-related products from carbon, such as graphene oxide and carbon nanotubes [5, 9, 14, 16]. The studies here sought to produce graphene nanosheets that were several layers thick, avoiding any agglomerated carbon nanostructures on the surfaces of the graphene [1, 10]. Each study used some variation of a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser. This is pulsed to ablate the surface of the graphite used [14]. The important parameters for the laser are the laser wavelength, repetition rate of pulsing, and the duration of a pulse. An example of one experimental setup for LP-PLA is shown in Their laser used ablated the graphite suspension at varying laser energies while the suspension was kept mobile by magnetic stirring, seen in **Figure 6(b)**.

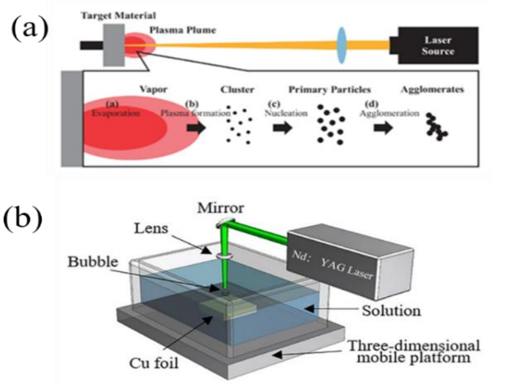

Figure 6. (a) Schematic of the Pulsed Laser Ablation process. This displays the general setup for production of nanoparticles. **(b)** Setup of LP-PLA, using an Nd:YAG laser to ablate the graphite target. This image from the study by Ren et al. has the distinction of having graphite in solution along with a copper substrate on which to deposit the produced graphene nanosheets. Images **(a)** from [14], **(b)** modified from [15].

5.2 Studies of LP-PLA

A benefit of LP-PLA is that it is a simple and relatively quick procedure. It can be difficult to control the exact kind of graphene made [5], but it is possible to understand the effects of the wavelength [1] and energy [15] of the laser used, the type [1] and concentration [10] of the liquid ablation medium used, and the composition of the target on the final product [1].

Zamiranvari et al. used graphite plates [10], while Ren et al. used graphite flakes made into a solution with deionized water [15]. Jalili et al. started with several target types and analyzed them based on their ability to make graphene and to make good quality graphene [1]. They first performed a five-minute test ablation with two types of flexible graphite, designated FG1 and FG2, which had SiO2 as part of the composition. Nuclear graphite was a third target type investigated in this test. Each flexible graphite yielded graphene nanosheets, while the nuclear graphite generated other carbon nanostructures when ablated [1]. From this test, they chose to use only the flexible graphite target. When comparing the Raman spectrum of the graphene produced using the FG1 and FG2 samples, they found that the I_D:I_G ratio was higher for the FG2, indicating a higher degree of defects in that graphene [1].

The same group of researchers also investigated the effect of different laser wavelengths on their selected targets. 1064 nm penetrated deeper below the target surface and increased the ablation efficiency, but ablated mass per pulse increased and unwanted particles formed on the surface of the nanosheets. 532 nm wavelength did not produce any unwanted particle formation on the surface [1]. Ren et al. changed the energy powering their laser and they found that for more laser energy, the morphology of deposited nanosheets was more complete, with fewer defects, more layers, and more uniform sheets over several micrometers [15]. **Figure 7** shows the HR-TEM images the group generated for few-layer graphene, showing the increase in the number of layers for increased laser energy. In their analysis of this phenomenon, the researchers stipulate that both the pulsed laser light and increased energy cause formation of more carbon plasma in the aqueous solution which is converted to more micron-sized graphene [15].

The team in Ren et al. carried out their LP-PLA process in de-ionized water alone [15]. The researchers in Jalili et al. found that acetone was the only liquid which resulted in a high-quality nanosheet, as it gave a higher molecular dipole moment compared to de-ionized water, which made for a stronger repulsive force between graphene layers and led to no agglomeration of particles [1]. Zamiranvari et al. worked with the cationic surfactant cetyltrimethylammonium bromide (CTAB) to understand its effect on the nanosheets produced [10]. Like Jalili et al., they chose a liquid which would provide separation of graphene from the graphite source, breaking apart the Van der Waals forces holding the two together. However, in using CTAB, they learned about the effect of CTAB on their LP-PLA process by adjusting the concentration of the liquid between 0.02 M and 0.1 M. The group found that increasing the concentration of CTAB led to a denser ablation environment and more pressure for the laser-generated plasma plume. They reached too high of a pressure for a concentration of 0.08 M CTAB, at which point the nanosheets that formed began to aggregate and break into a lower-quality graphene with other carbon-containing nanostructures. They determined the optimal concentration to be 0.06 M CTAB through several characterization methods. XRD analysis for the 0.06 M-produced graphene gave the lowest peak intensity, where the researchers attributed their more crystalline samples to other nanostructures present, such as fullerites and carbon oxides [10]. The degree of defects was determined by Raman spectroscopy, which gave larger I_D:I_G ratios for the graphene from concentrations both above and below 0.06 M. Furthermore, it was noted that at 0.06 M CTAB, graphene nanosheets were the dominant type of carbon nanostructure formed and these were lowest in defects compared to the graphene nanosheets prepared at other tested concentrations of the liquid medium [10].

The studies by Jalili et al. and Zamiranvari et al. collected the graphene supernatant from a suspension produced through LP-PLA [1, 10], but Ren et al. used a copper substrate to collect graphene nanosheets [15]. For their experiment, the copper substrate led to a major difference by providing a surface for the graphene to adsorb onto and catalyzing graphitization of carbon.

By changing the laser parameters, liquid medium, and even providing a substrate for graphene to land on, the mentioned studies have found ways to increase the efficiency of the LP-PLA process and the quality of graphene produced.

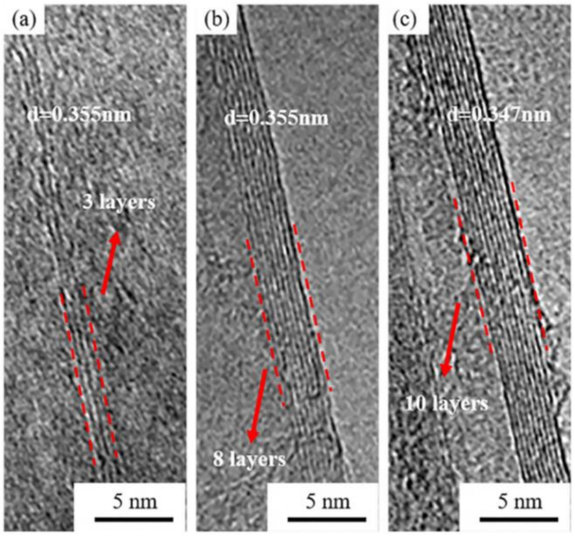

Figure 7. High-Resolution TEM images of few-layer graphene prepared through Liquid-Phase Pulsed Laser Ablation. These come from Ren et al. for graphene deposited on a copper substrate for laser energies of **(a)** 0.1 J, **(b)** 0.2 J, and **(c)** 0.3 J. As the laser energy was increased, the researchers discovered they were making more layers of graphene. Images from [15].

6. Summary

Graphene in single or few-layer sheet form can be viewed in terms of its quality by the given processing route to enhance and gain a better understanding of that method. The shared factor for making graphene from a graphite source through top-down methods is to break down the existing structure held together with weak Van der Waals bonds. Several routes to accomplish this are possible, using electrochemical cells as a medium for exfoliation, exfoliation in liquid actuated through agitation, or by ablation of graphite with a pulsed laser. Each of these methods are subject to improvement for the liquid used [1, 4], the concentration of the medium [8, 10], the parameters related to post-processing [1, 11, 15], or an alteration to the process itself [6, 11, 15]. An understanding of the principles behind the process and characterization of the synthesized graphene product are both essential to more refined processing.

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Conflict of Interest

The author declares no conflict of interest.

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