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Synthesis of 2D materials in arc plasmas

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Abstract

In this article we review recent efforts focused on synthesis of two-dimensional (2D) materials in an arc-plasma based process with particular focus on graphene. We present state-of-the-art experimental data on various attempts to employ the arc plasma technique for the graphene synthesis and consider growth mechanisms including precipitation, surface-catalyzed processes and a substrate-independent approach. The potential of arc synthesis for the growth of other types of 2D materials and future prospects are discussed.

Keywords: plasma nanoscience, plasma-based synthesis of 2D materials, graphene

(Some figures may appear in colour only in the online journal)

1. Introduction

Plasma discharges are traditionally utilized for deposition of thin films of various materials as well as for synthesis of different micro and nanostructures. [1–3] Traditional methods utilizing plasmas at synthesis include plasma-enhanced chemical vapor deposition (CVD), cathodic and magnetron sputtering, vacuum arc deposition etc [1–3].

One use of plasmas is in the vicinity of synthesis substrates (e.g. in plasma-enhanced CVD) in order to improve properties of the surface-grown films/structures and reduce temperatures of synthesis substrates.[1, 2, 4] The benefits of the plasma-enhanced CVD techniques result from significant enhancement of the reactivity of the species involved in the surface synthesis when plasma is used. These species are typically produced by glow discharge initiated in the vicinity of the growth substrate. With respect to the deposition of thin micron-sized films, utilization of plasma-enhanced CVD means synthesis temperature can be kept in the range 300–400 °C as opposed to 1000–2000 °C for conventional CVD, improves adhesion of the films to the substrate and in many cases provides higher deposition rates (e.g. TiN, TiC, TiO_2, Al_2O_3 etc) [1–3]. With respect to nanostructure synthesis, application of plasma-enhanced CVD for synthesis is also widely known to improve quality, reduce synthesis temperature, control of the alignment etc [5, 6]. Recent experiments on plasma enhanced CVD synthesis of graphene demonstrate the reduction of synthesis temperature to about 500–650 °C from about 1000 °C at conventional CVD [7, 8].

Plasma discharges (vacuum arcs, discharges in liquids, high-pressure arcs in different gases, microwave discharges etc) can be also utilized for gas-phase synthesis of various types of free-standing nanoparticles in the discharge volume and its vicinity [3, 9–14]. The variety of nanostructures that can be synthesized using these methods includes carbon nanotubes, carbon onions, fullerens, nanohorns, graphene etc [9–11, 15–18]. Among several methods of production of carbon nanoparticles and, in particular, carbon nanotubes, high-pressure arc discharge has a number of important advantages. Firstly, the arc discharge method yields highly graphitized tubes with very small defects because the synthesis occurs in the near proximity of a high-pressure arc column which is characterized by very high temperatures >3000–4000 K [11, 19–22]. Secondly, nanostructures produced in the arc usually demonstrate a high flexibility, thus eventually demonstrating higher strength characteristics [10, 11, 23]. These advantages of the arc method have resulted in extensive application of arcs for synthesis of single wall carbon nanotubes both in research labs and industry [10, 11, 24–26].

In this article we review different approaches to synthesize 2D nanomaterials with a particular focus on production graphene in arc discharge. We will present available experimental data on the synthesis of graphene in an arc, and discuss growth mechanisms and advantages of the arc-based approach. The article will combine a review of published materials as well as the presention of new data (see section 3.3).

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2. Types of graphene and conventional plasma-free synthesis methods

Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice [27]. This new material combines aspects of semiconductors and metals and could be a leading candidate to replace silicon in applications ranging from high-speed computer chips to biochemical sensors. Potential applications of graphene cover a huge spectrum of problems including fast transistors, stretchable/foldable electronics to optical devices, biosensors, energy storage applications etc [28–42].

Single-layer graphene was synthesized using regular Scotch tape by mechanical exfoliation of layers from bulk graphite by Geim and Novoselov in 2004 [27, 43, 44]. Six years later authors of these works were awarded the Nobel Prize in Physics 'for groundbreaking experiments regarding the 2D material graphene' [45]. Since the original synthesis method was extremely expensive and inefficient, this triggered an active search for more efficient ways of graphene production. Among other methods created in following years one can mention epitaxial growth on SiC, CVD, chemical exfoliation, combustion synthesis etc [32, 46–51]. Generally, these methods allow the synthesizing of two types of graphene, namely large-area graphene films (pristine graphene) and micron-sized graphene platelets.

The first type of graphene, namely large-area pristine graphene films, is synthesized using CVD, and currently utilized for ultra-high-speed, low-power graphene-based electronics and optical devices [30–34, 36–38, 52]. The graphene films are first synthesized on the hot substrates of transition metals and then transferred to the final substrate, e.g. Si wafer or transparent electrode. One of the central challenges of this research area is the synthesis of high-quality continuous and uniform graphene films on large areas (>8 inch in diameter) and the reduction of damage to the graphene film at the transfer to the final substrate [32, 52].

Pristine graphene film growth is strongly governed by the degree of carbon solubility in substrate material [38, 52]. Two growth mechanisms can be distinguished in this respect, namely precipitation growth and surface-catalyzed growth. The graphene growth is driven by the precipitation process when the substrate is made of materials in which carbon is soluble, e.g. Ni, Co, Pt, Ru [38, 52–54]. In this case the carbon atoms first dissolve in the substrate material preheated typically to 800–1000 °C and then precipitate on the substrate surface whilst cooling down as carbon solubility decreases with temperature [53]. Carbon atoms precipitated on the substrate surface form a graphene layer. Such graphene films are usually limited to the grain size of the substrate material and may contain many layers.

The surface-catalyzed mechanism of graphene growth is employed when materials with low carbon solubility are utilized as a growth substrate, e.g. Cu [32]. In this case carbon atoms cannot penetrate inside the substrate but are able to diffuse along the surface instead. Experiments indicate that if the Cu substrate is heated to about 1000 °C, carbon atoms attach to each other in a honeycomb lattice of sp^2 bonded atoms and form a continuous graphene layer [32]. The complete graphene layer becomes inert for the attachment of new carbon atoms and thus synthesis is typically limited to the production of a single layer graphene film. The crystal structure and polishing of the substrate play important roles in the quality, uniformity and growth rate of graphene films [55, 56].

The second type of graphene, graphene platelets is usually characterized by several layer thick (2–20 nm) graphene pieces having characteristic sizes in the micron/sub-micron range [57–59]. Potential applications of graphene platelets include thermal management, nanocomposites (e.g. electrically and thermally conductive plastics, mechanical reinforcement) and electrochemical energy storage devices (ultracapacitors and fuel cells) [58, 60]. Currently, graphene platelets are mainly produced by the chemical exfoliation method, where chemicals are utilized to separate the graphene sheets from the piece of graphite [57, 58]. The current production capability is quite limited and is estimated to be around hundreds of tons of material annually worldwide [58, 60].

3. Arc synthesis of graphene

Generally, arc discharge can be utilized with any mentioned above graphene synthesis approach as a source of atomized carbon flux. However, advantages related to utilization of an arc for the synthesis extend far beyond simply utilization of the arc source as a raw carbon material supply. Since arc-produced carbon vapor is characterized by high purity at extremely high ablation rates, the utilization of arc sources is advantageous for industrial-scale production and can yield high quality graphene with no structural defects and great crystallinity [11, 61]. In addition, the arc method has especially high potential for the manufacture of graphene platelets in which spatial uniformity and stability of the carbon flux are less important than that for the production of large-area pristine graphene films. Below, we will present state-of-the-art experimental data demonstrating the benefits of the arc-based approach for graphene synthesis.

3.1. Synthesis on substrates with high carbon solubility: precipitation mechanism

The experiments on precipitation graphene growth in an arc on the substrates with high carbon solubility are reported in [13, 62–66]. These experiments utilized an anodic arc operating at 500 Torr Helium in the presence of an external magnetic field produced by a permanent magnet. It was observed that the presence of the magnetic field led to the attraction of the arc column towards the magnet as shown in figure 1. Graphene flakes of about several to tens of μm in diameter were found in the deposit grown on the magnet surface after the arcing primarily on the inner part of the deposit facing the magnet. The Raman spectra of the obtained graphene flakes are shown in figure 2 indicating the presence of several-layer-thick graphene flakes. Raman spectra show the absence of the D-peak at 1350 cm^{-1} indicating a very low level of defects and a high purity of the flakes [67, 68]. The ratio intensities of

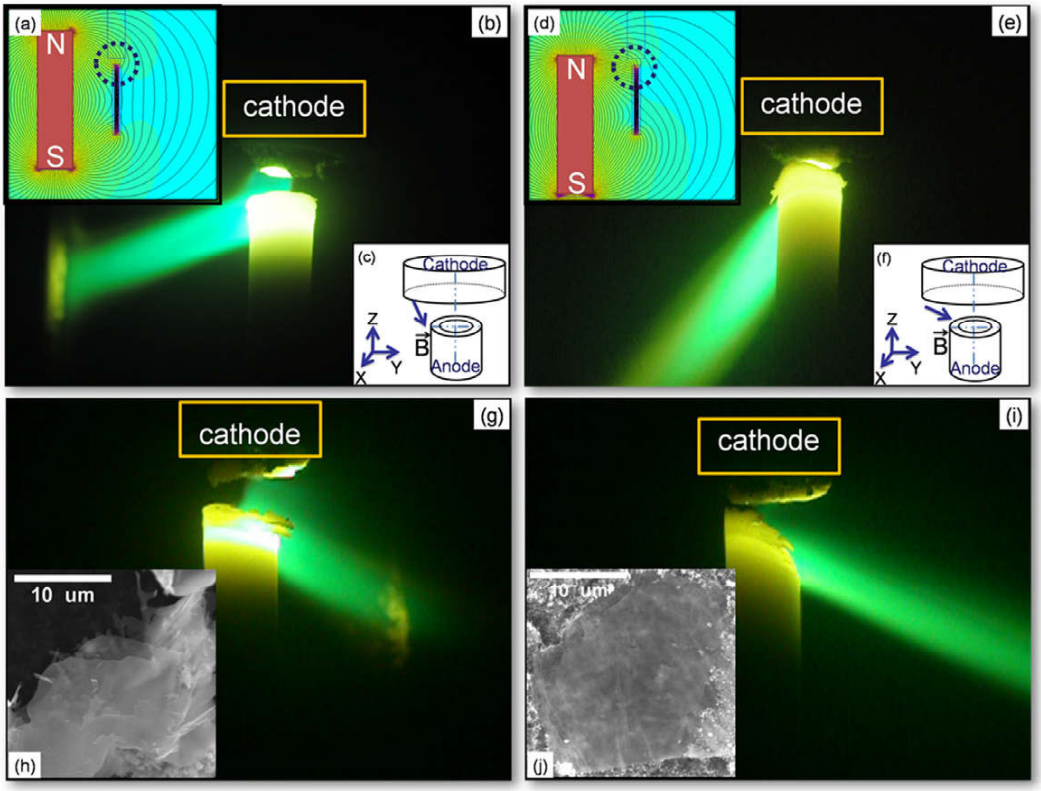

Figure 1. (*a*) Distribution of magnetic field; (*b*, *g*) photographs of arc plasma jets and (*c*) schematic diagram of the relative position of electrodes. (*d*, *e*, *i*, *f*) Same images for other magnet positions with respect to arc electrodes. (*h*, *j*) Typical SEM images of produced graphene flakes. Reproduced with permission from [65], Copyright 2011 IEEE.

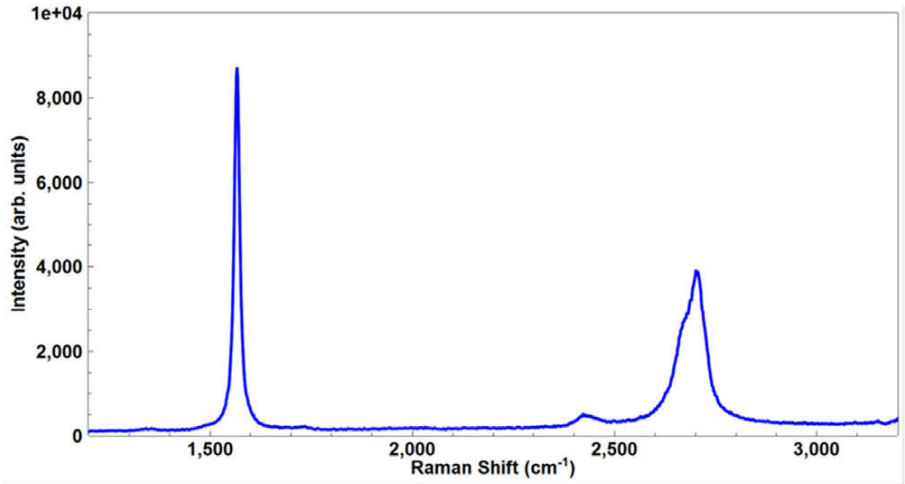

Figure 2. Raman spectra of arc-produced graphene at precipitation growth on Ni-containing substrates.

G and 2D (or G′) [67, 68] peaks indicate that the number of layers in the synthesized flakes was >2.

The results of these experiments can be interpreted as follows. Since both magnet material (Alnico 8, >10% of Ni) and the anode (molar ratio C:Ni:Y = 56:4:1) contain a notable Ni fraction which is characterized by high solubility of carbon atoms, we may speculate that synthesis is driven by the precipitation process. The magnetic field created by the permanent magnet plays the following role in the synthesis. First, it directs the arc column towards the magnet causing delivery of the raw ionized carbon flux to the substrate (magnet). Secondly, the magnet was heated by the arc locally in the

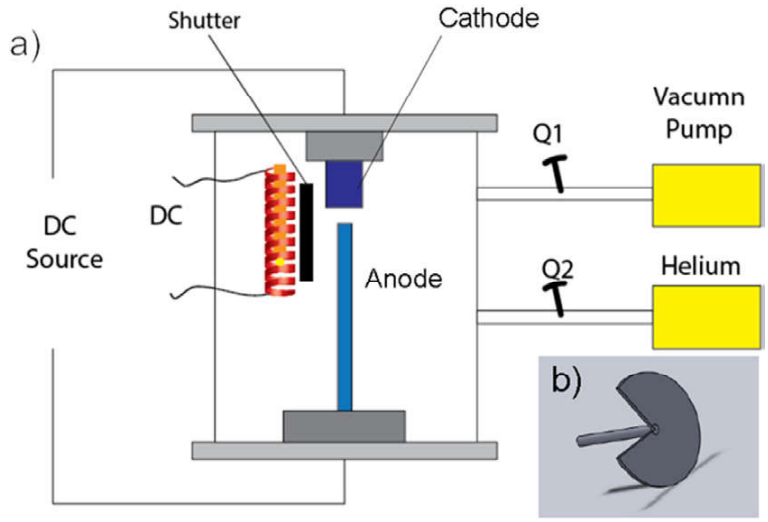

Figure 3. (*a*) Schematic of the set-up of the arc discharge system; (*b*) shutter used to control exposure time of the substrate to the carbon flux from the arc.

vicinity of the arc-magnet contact point (see figure 1). As result, the precipitation growth mechanism similar to that described in the previous section for the case of the CVD process may be responsible for graphene production observed on the surface of the magnet. Carbon atoms and ions reaching the hot magnet zone were adsorbed in the near-surface layer of the magnet and then precipitated to the surface during the cooling stage after discharge interruption, which led to formation of graphene film on the magnet surface. Also, some graphene flakes were potentially synthesized on the surface of Ni droplets originated from the anode and delivered through the arc zone to the magnet surface.

3.2. Synthesis on substrates with low carbon solubility: surface-catalyzed mechanism

The experiments presented in this section utilized materials with low carbon solubility for the substrate (copper foil) and electrodes (pure carbon rods) [69]. Solubility of the carbon in copper around the Cu melting point (1085 °C) is very low (<0.008 weight %) compared to, for example, Ni (~0.6 weight % at 1326 °C) traditionally utilized for synthesis driven by the precipitation process [53]. Therefore, we conclude that in this case the synthesis was driven by surface-catalyzed processes rather than by precipitation.

The rectangular piece of 0.1 mm thick Cu foil (1.5 mm × 14 mm) was pre-heated by the resistive wire wound around the substrate. The substrate was exposed to the carbon flux produced by the arc for <100 ms which was controlled by a shutter shown schematically in figure 3. The anodic arc at 500 Torr of helium with the arc current in the range 70–80 A was utilized at synthesis. The distance between the substrate and the arc source was about 1.5–2 cm. No magnetic field was used and both arc electrodes were made of pure POCO EDM-3 graphite rods. Figure 4 shows the photo of the arc discharge taken from the front window of the chamber. The temperature of the substrate was simulated in COMSOL software as described in more detail in [69].

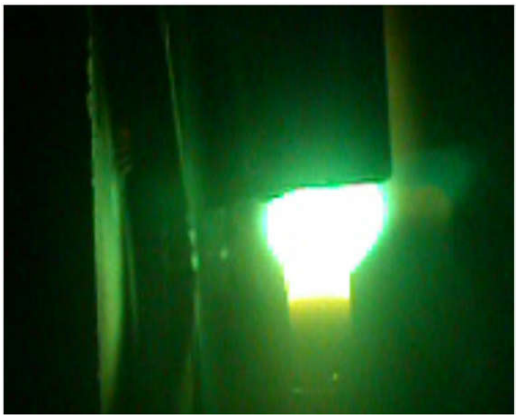

Figure 4. Photograph of the arc at surface-catalyzed graphene synthesis.

Graphene synthesis was observed in a very narrow temperature range around Cu melting point as one can see in the Raman spectra presented in figure 5. The pronounced 2D peak was observed only for $T \sim 1350$–1358 K (1077–1085 °C) while lower temperatures led to the synthesis of amorphous carbon structures only. An SEM image of the graphene film synthesized at this temperature range is shown in figure 6(*a*). Note, the darker zone seen in the middle of the SEM image is caused by the pore, the formation of which on the substrate was typical around the Cu melting point. The Raman image of the same location is shown in figure 6(*b*). One can see that the D-peak was significantly more pronounced compared to that observed for the synthesis on substrates with high carbon solubility (see figure 2) which can be explained by the relatively small size of the graphene flakes (~200 nm) and proximity of the flake edges [70].

It should be noted that the existence of the very low but nonzero solubility of carbon in copper suggests that it is unlikely to have a pure surface-catalyzed process, and the

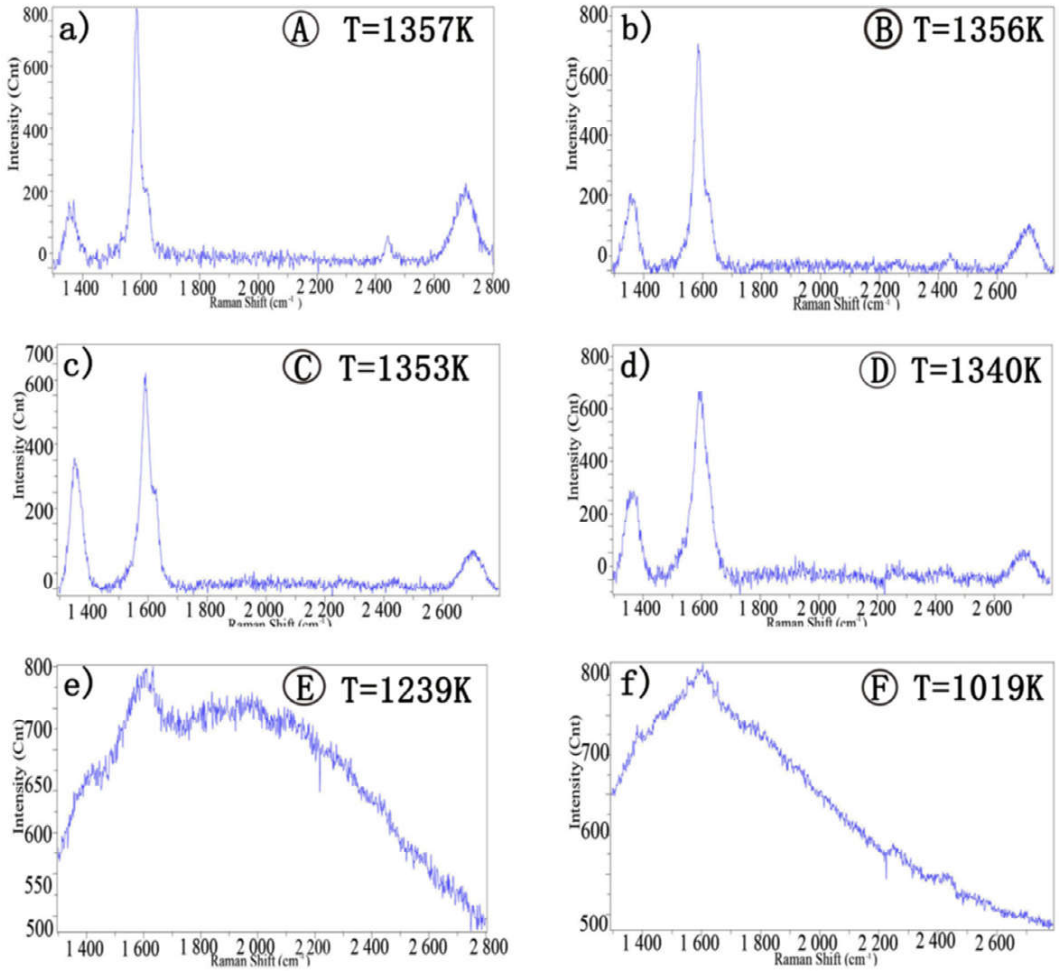

Figure 5. Raman spectrum along the substrate with different lengths from the melted point.

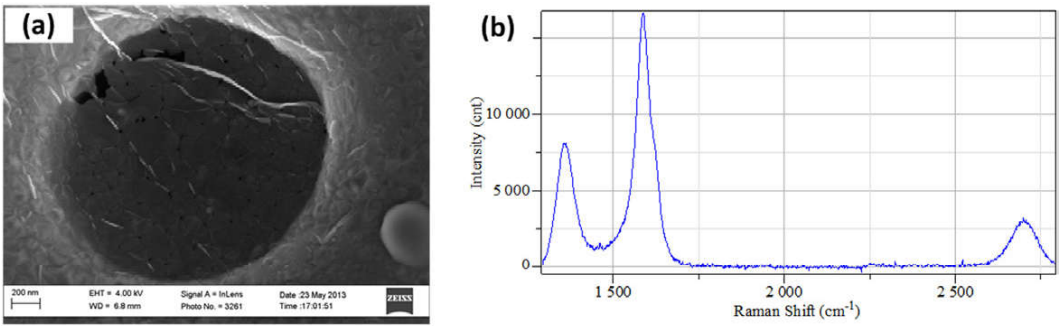

Figure 6. (*a*) Typical SEM image of graphene grown on Cu substrate (surface-catalyzed process) and (*b*) Raman spectrum of the corresponding area.

precipitation mechanism may have some contribution in graphene production as well.

3.3. Substrate material independent growth of non-oriented graphene platelets

Non-oriented graphene platelets were synthesized in lower background pressure, namely at residual air pressure of about 0.1 Torr. The POCO EDM-3 graphite was used for the electrodes material. The anode and cathode had diameters of 3 and 12 mm, respectively. Electrodes were separated about 4–5 mm from each other and the sample was located about 5 cm radially from the electrodes. The sample was preheated up to 1000 °C in the experiments. Arc discharge durations <1 min and arc currents about 70 A were utilized.

Typical Raman spectra and SEM images of the graphene flakes synthesized using this approach at $t = 750$ °C are shown in figure 7. One can see that the graphene flakes represented

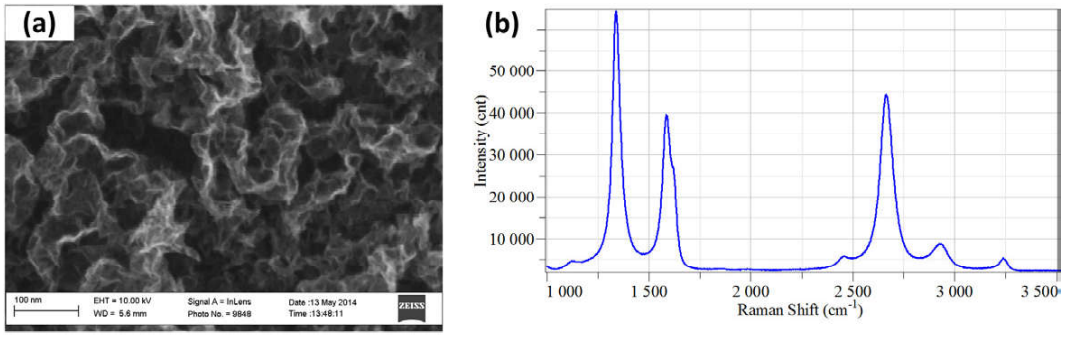

Figure 7. (*a*) Typical SEM image; and (*b*) Raman spectrum of the graphene platelets synthesized in the substrate-independent process.

have an entangled web-like structure. Raman spectra indicate the presence of the pronounced 2D peak having an intensity close to that of the G-peak, which indicates that on average the number of layers is ≥2. Note, the large D-peak is caused by random orientation and the small size of the flat graphene areas (~tens of nm) [70]. The elemental analysis conducted using energy dispersive x-ray spectroscopy indicates a very low level of impurities <0.5%. Ultimate graphene synthesis rates up to 0.5 g min^{-1} were achieved with 90% efficiency of the electrode material utilization. The substrate temperatures >700 °C were found to be favorable for the synthesis, while temperatures below 700 °C yielded amorphous carbon structures without the 2D-peak in Raman spectra. Similar synthesis techniques utilizing arc discharge for the synthesis of bulk non-oriented graphene flakes were presented in works [71, 72].

Note that different materials of the substrate were utilized at synthesis such as Si and SiO wafers, Mo foil, quartz and alumina ceramics. Relatively thick coatings (a fraction of a millimeter) were obtained in the experiments. The coatings contained entangled non-oriented graphene flakes, regardless of the substrate material. It is important to note that the upper layers of the graphene flakes did not make contact with the substrate, but instead grew directly on top of the existing flakes. Therefore, we identify this synthesis approach as substrate-independent.

4. Gas-phase graphene synthesis

Recently, synthesis of free-standing graphene sheets in the plasma-based process in the gas phase was presented [16, 17, 73, 74]. This process involves nucleation directly in the plasma reactor volume in contrast with heterogeneous nucleation at the nucleus on surfaces considered in previous sections. Tatarova *et al* [73] utilized microwave discharge initiated in flow containing a mixture of argon and ethanol vapor at atmospheric pressure. After passing the discharge zone, the decomposed gas mixture enters volume with the temperature controlled by the cryostat system in the range of about ≤100 °C. Solid products (including graphene and other nanostructures) are collected on the membrane filters located following the cryostat. It is interesting to note that this approach does not utilize any preheated grown substrate as opposed to conventional synthesis methods considered above. Instead, authors claim that graphene synthesis occurs in the volume after decomposed gas products leave the hot discharge zone and enter the cryostat system. Membrane filters serve as a substrate collecting the graphene flakes. Even though authors do not specify filter temperature, one can assume it was around room temperature, so it is highly unlikely that surface-catalyzed or precipitation processes are involved in the synthesis. In contrast, it can be speculated that graphene is synthesized in a purely volumetric process. The mechanism involved in the synthesis is not clear and warrants future investigation. Some authors indicate production rates up to 500 g h^{-1} [74]; however, ultimate production capability of this approach is yet to be determined in order to understand its practical potential.

5. Other types of 2D materials

Breakthrough experiments conducted by Geim and Novoselov on exfoliation and characterization of graphene triggered tremendous interest in the field of 2D materials [27, 75]. Physical properties of 2D materials cover a very large range (e.g. electrical conductivity varies from graphene that conducts extremely well to semiconducting molybdenum disulfide MoS_2 and insulating boron nitride h-BN) which enables a variety of potential applications from electronics to optical devices and biosensors [29, 40, 41, 76–79].

Currently, utilization of arc discharge for 2D material synthesis is in its infancy, while CVD techniques are primarily utilized for that purpose [32, 75, 80]. At the same time, extensive previous knowledge on the application of arcs for the growth of thin films of various compositions certainly creates a unique opportunity for the utilization of arcs for 2D material growth [3]. In addition, few available works on the utilization of arcs for gas-phase functionalization of carbon nanotubes and doping graphene with boron, nitrogen and hydrogen indicate a high potential of gas-phase functionalization *in situ* during the arc nanostructure synthesis [71, 81]. Future research should pave the way for the utilization of arc discharge for synthesis of various types of pure and functionalized 2D materials, and identify the ultimate role of arc discharge in research and industrial application of 2D materials.

6. Concluding remarks

In this work we reviewed state-of-the-art arc-based processes for synthesis of 2D materials with particular focus on the

synthesis of graphene. We presented available experimental data on the utilization of the arc discharge for graphene synthesis on substrates with high and low graphene solubility driven by precipitation and surface catalyzed processes, respectively. Even though arc discharge can be utilized in many synthesis processes as a source of carbon vapor, its potential extends far beyond that. Utilization of different discharge electrode materials and background gases demonstrate the potential for synthesis of different types of 2D materials and application-specific gas phase functionalization. In addition, utilization of highly-reactive ionized species and high temperatures at arc synthesis ensures high overall material quality along with reduced substrate temperature requirements. Finally, easy scalability of the synthesis process by increasing the arc current shows the potential of the arc method for large industrial-scale synthesis. Ultimate properties of the arc-based synthesis, such as production yield, efficiency and material purity, are the subject of future research.

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