TOPICAL REVIEW

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To cite this article: Carles Corbella *et al* 2022 *Nanotechnology* **33** 342001

IOP Publishing Nanotechnology
Nanotechnology 33 (2022) 342001 (20pp) https://doi.org/10.1088/1361-6528/ac6bad

Topical Review

Nanosynthesis by atmospheric arc discharges excited with pulsed-DC power: a review

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Received 13 January 2022, revised 14 April 2022
Accepted for publication 29 April 2022
Published 31 May 2022

Abstract

Plasma technology is actively used for nanoparticle synthesis and modification. All plasma techniques share the ambition of providing high quality, nanostructured materials with full control over their crystalline state and functional properties. Pulsed-DC physical/chemical vapour deposition, high power impulse magnetron sputtering, and pulsed cathodic arc are consolidated low-temperature plasma processes for the synthesis of high-quality nanocomposite films in vacuum environment. However, atmospheric arc discharge stands out thanks to the high throughput, wide variety, and excellent quality of obtained stand-alone nanomaterials, mainly core–shell nanoparticles, transition metal dichalcogenide monolayers, and carbon-based nanostructures, like graphene and carbon nanotubes. Unique capabilities of this arc technique are due to its flexibility and wide range of plasma parameters achievable by modulation of the frequency, duty cycle, and amplitude of pulse waveform. The many possibilities offered by pulsed arc discharges applied on synthesis of low-dimensional materials are reviewed here. Periodical variations in temperature and density of the pulsing arc plasma enable nanosynthesis with a more rational use of the supplied power. Parameters such as plasma composition, consumed power, process stability, material properties, and economical aspects, are discussed. Finally, a brief outlook towards future tendencies of nanomaterial preparation is proposed. Atmospheric pulsed arcs constitute promising, clean processes providing ecological and sustainable development in the production of nanomaterials both in industry and research laboratories.

Keywords: anodic arc discharge, nanomaterials, plasma technology, pulsed power

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

1. Introduction

Plasmas are ionized gases, which show intense exchange of matter and energy with neighbouring surfaces. The controlled flux of incident plasma species enables growth of films and nanoparticles (Lieberman and Lichtenberg 2005, Baranov *et al* 2017). Arc discharge is a very interesting plasma regime basically characterized by high currents, up to several kA, sustained at low voltage values, of the order of tens of volts. Such plasmas are suitable for many applications in both vacuum and atmospheric pressure ranges, like discharge lamps, welding, and material processing (Boxman *et al* 1995, Keidar and Beilis 2018). Arcs in particular show features very exciting for further research, like the interplay between local

hot and cold plasma regions, and instabilities in the form of spots at either cathode or anode surfaces (Jüttner 2001).

After the discovery of carbon fullerenes by Kroto *et al* (1985), Iijima pioneered the synthesis of carbon nanotubes by means of atmospheric arc technique (Iijima 1991). Since then, milestones like the arc production of fundamental nanomaterials such as boron nitride nanotubes (BNNT) (Chopra *et al* 1995) and molybdenum disulphide nanoparticles (Chhowalla and Amaratunga 2000) have boosted the progress of plasma nanotechnology. This research field has become ubiquitous due to its multidisciplinary character, for instance in optoelectronic applications (Li and Zhu 2015, Lin *et al* 2016, Yang *et al* 2019, Kumar *et al* 2022), smart materials (Golberg *et al* 2007, Levchenko *et al* 2018), medicine, (Zhang *et al* 2017, Bazaka *et al* 2019) and nanomaterials modelling (Momeni *et al* 2020). In parallel, there is an urgent need to improve the quality and synthesis reproducibility of low-dimensional materials. Indeed, serious concerns and scepticism have been raised regarding the quality of the showcased materials (Kauling *et al* 2018, Bøggild 2018). In this regard, traditional techniques must be improved and new recipes should be developed to meet the stringent demands that only pure samples of nanomaterials can fulfil.

Plasma constitutes an excellent scenario to synthesize and/or modify nanomaterials with tailored properties. The wide range of plasma parameters provide adequate knobs to tune the physical and chemical properties of the processed nanostructures, thereby enabling the synthesis of top-quality and ultra-pure nanomaterials showing the desired performance. The extraordinary service that plasma technology has been offering to processing of nanoparticles and nanomaterials is reviewed in a number of excellent articles (Cheng *et al* 2010, Boufendi *et al* 2011, Han *et al* 2018, Vasudevan *et al* 2019, Zietz *et al* 2020, Vandenabeele and Lucas 2020).

Pulsed plasmas suppose an even better framework due to the additional parameters required to program a periodically excited discharge. An immediate effect is the tuning of the physical mechanisms governing a discharge, like ionization rates and diffusion processes (Anders 2004). Thus, a more accurate control of the discharge is achieved by setting the adequate pulse parameters of the feeding signal. In contrast to DC power and AC power, pulsed-DC power confers a more flexible scenario in the working conditions at the plasma-material interface (figure 1) (Arora and Sharma 2014). In fact, given a specific signal waveform, plasma parameters can be controlled by adjusting peak values of voltage and current, pulse duration and frequency. Concerning the topic reviewed here, pulsed arc discharges is a research field with a huge potential in nanomaterial production. While significant steps have been made in maturing and upscaling film deposition by cold, low-pressure pulsed plasmas (Wertheimer *et al* 1996, Heggemann *et al* 2007, Bräuer *et al* 2010, Corbella 2014, Bobzin *et al* 2017), relatively little effort is shown on nanosynthesis by pulsed arcs held near atmospheric pressure, either in gas phase (Corbella *et al* 2019c) or in liquid phase (Kim *et al* 2021). It is not surprising that pulsed arc nanosynthesis is attracting more and more interest within the materials science community after the versatility and flexibility offered by this technique.

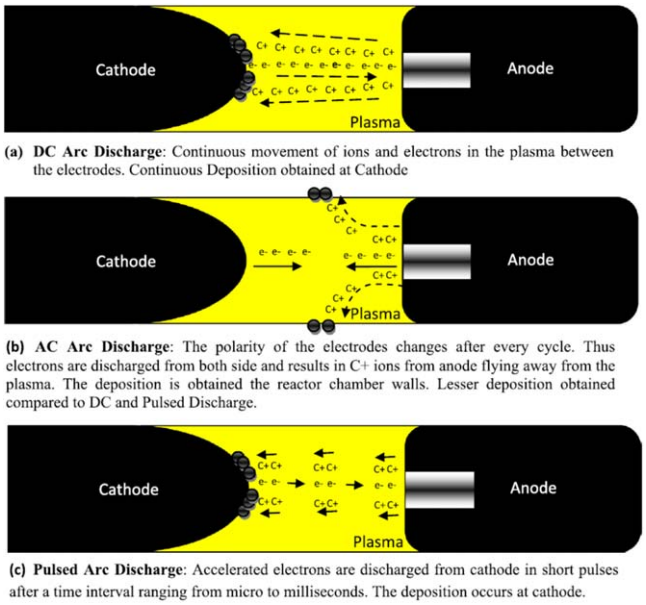

Figure 1. Schematic representation of species transport between a hollow anode and cathode in anodic arc discharge in (a) DC, (b) AC, and (c) pulsed-DC modes aimed to grow carbon nanostructures. Deposition on chamber walls is also feasible in scenario (a) due to significant growth rate of particles that are transported in the radial direction. The cavity of the anode is filled with catalyst powder to promote carbon nanotube growth. Reprinted from (Arora and Sharma 2014), Copyright © 2014 Elsevier B.V. All rights reserved.

The present review starts by briefly comparing pulsed plasma techniques oriented to surface and in-volume nanosynthesis. Following a short summary about nanotechnology applications of glow and arc discharges in pulsed form, the state of the art and main challenges in atmospheric arc nanosynthesis are discussed. After these introductory sections, up-to-date research focused on pulsed arc methods to produce nanosized materials is analysed. The article concludes with a summary and outlook listing future milestones of this promising tool to create new nanomaterials.

2. Pulsed plasmas and nanotechnology

This section provides insight into the main plasma methods used in nanotechnology for the fabrication of nanostructured materials, either in thin film form or as stand-alone nanomaterials. The objective here is to chart the area of plasma applications, specifically using pulsed energy, in terms of deposition parameters and industrial needs.

2.1. Surface nanosynthesis by non-thermal plasma—glow discharges and vacuum arcs

As opposed to the arc regime, glow discharges are characterized by plasmas excited at high voltages and relatively low currents (Lieberman and Lichtenberg 2005). Pulsed glow discharge in vacuum is a well-developed, mature technology.

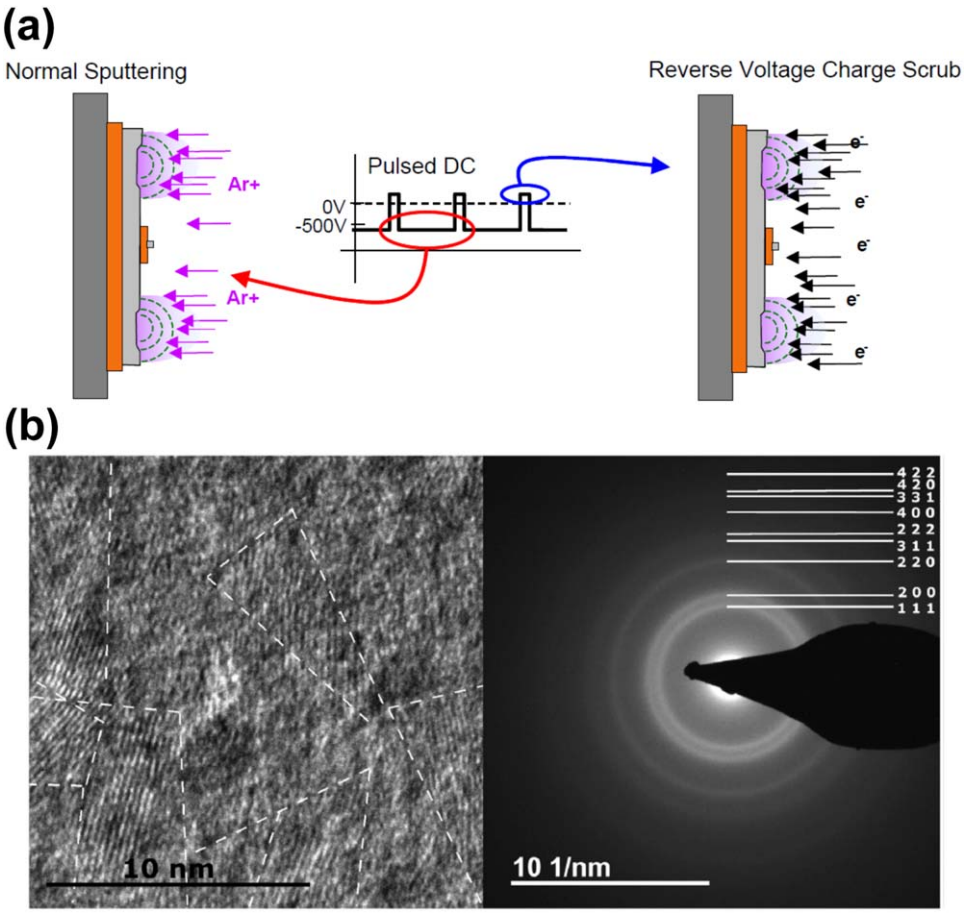

Figure 2. (a) Correspondence between waveform phases and species bombardment in pulsed-DC magnetron sputtering. Reprinted from Sproul *et al* (2005), Copyright © 2005 Elsevier B.V. All rights reserved. (b) High-resolution transmission electron microscopy (HRTEM) image (left) and selected area electron diffraction (SAED) pattern (right) of a (Ti,Zr)C:H/a-C:H nanocomposite film deposited by reactive HiPIMS. Target arcing and poisoning due to reactive gas are prevented with pulsed plasma techniques. Reprinted from Poltorak *et al* (2020), © 2020 Published by Elsevier B.V.

In low-pressure plasma applications, the control over ion energy and ion bombardment onto processed surfaces (sputtering, deposition, or modification) plays a central role due to the reduced collision frequency among plasma species (Andujar *et al* 2003, Gahan *et al* 2012). The key point in optimizing pulsed plasmas in coatings and etching applications relies in the addition of 'knobs' available to modulate plasma parameters, which in turn affect material properties. This topic was analysed in detail from the physics perspective by Anders (2004). The frequency of the supplied power in pulsed discharges should be tuned according to the characteristic plasma frequencies. This review deals with pulsed plasmas with excitation frequencies of the order of 100 kHz or lower. Such a frequency regime is below the interval of typical ion plasma frequencies (1–10 MHz), thereby enabling the response of ions to changes in the voltage waveform. This window corresponds to the pulsed-DC power used in magnetron sputtering and plasma-enhanced chemical vapour deposition (PECVD) techniques both in research and in industry (50–350 kHz, 500–1500 V peak, 0.1–1 A m^{-2}).

Structures within a pulsed-DC glow discharge, like sheaths and ionization layers, evolve periodically with time, out of steady state and with much higher amplitude than in radiofrequency or microwave discharges (Bradley and Welzel 2009, Gahan *et al* 2012). Moreover, pulse repetition frequency is decisive on the shape (width and extension) of the energy distribution of the ions impinging onto the biased surface (Baloniak *et al* 2010, Corbella *et al* 2011). Waveform of pulsed-DC voltage in glow discharges consist usually of quasi-rectangular profiles with controllable duty cycle (figure 2(a)). High values in current and voltage, sometimes showing a bipolar overshoot in the voltage waveform, have been motivated to suppress arcing and to increase electron density, electron temperature, and ion bombardment (Sproul *et al* 2005, Berg and Nyberg 2005). This deposition technique has been very popular in the growth of hard ceramic materials, such as diamond-like amorphous carbon (DLC) films. In DLC-based film growth, besides plasma composition, intense ion bombardment onto the growing film is critical in determining excellent mechanical and tribological properties (Michler *et al* 1998, Robertson 2002, Andujar *et al* 2003). The increased process stability owing to the absence of arcing comes from the periodical neutralization of charges built-up at the cathode surface after completing each pulse cycle

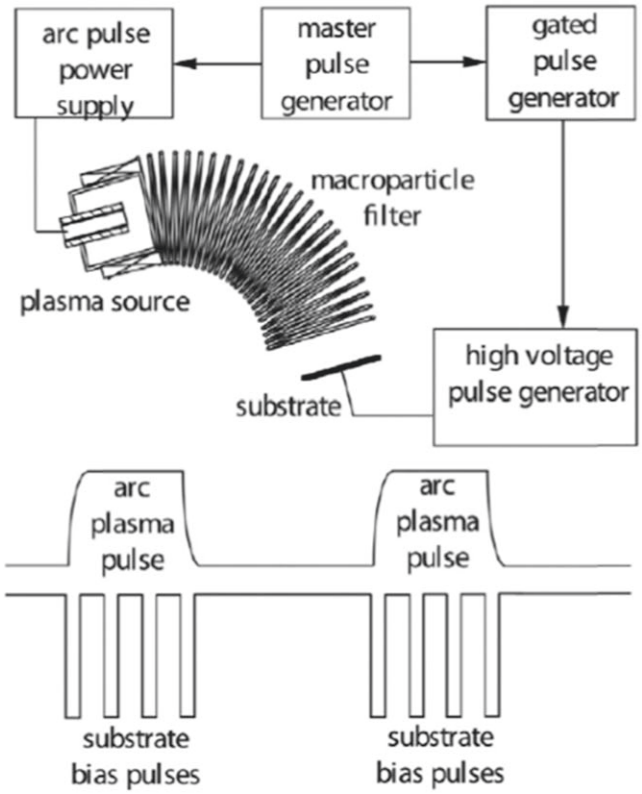

Figure 3. Sketch of a typical cathodic arc setup using a combination of pulsed arc bias and substrate bias to control the ion bombardment during film growth. Substrate biasing is a strategy used in plasma technology to deposit dense and hard films for protective coating applications. Reprinted from Anders (2014), Copyright © 2014 Elsevier B.V. Published by Elsevier B.V. All rights reserved.

(figure 2(a)). This feature confers ample margin for the flow rate of reactive gas without contamination/poisoning of a magnetron target. Deposition of metal-containing DLC films has been benefited from weaker poisoning of metal targets by reactive gas (Berg and Nyberg 2005). As a consequence, wide varieties of nanocomposite morphologies (granular, columnar, layered and dendritic) and of surface properties have been achieved (Corbella *et al* 2005). Nanocomposite structuring usually reports an increase in toughening and film adhesion to substrate (Pauleau and Thièry 2004, Zhang *et al* 2005).

Following the trend of using energetic pulsed plasmas to enhance the density and hardness of coatings, high-power impulse magnetron sputtering (HiPIMS) has been developed as an alternative to pulsed cathodic arc (Sarakinos *et al* 2010, Anders 2017, Brenning *et al* 2020). Both techniques show important similarities when it comes to the surface and physical properties of the deposited films (Anders 2014). HiPIMS technique (0.01–5 kHz, <1% duty cycle, ≈1 W cm^{-2} average, ≈1–100 kW cm^{-2} peak, $n_e \approx 10^{19}$ m^{-3}) is suitable to prepare metallic (Wu *et al* 2018) and ceramic (Evaristo *et al* 2020, Poltorak *et al* 2020) coatings with tailorable properties (figure 2(b)). Vacuum cathodic arc is also very useful to obtain hard multicomponent films (Monteiro *et al* 1999, Chaus *et al* 2014). An important issue in pulsed vacuum arc (≈10^6 kW cm^{-2} in cathode spots, $n_e \approx 10^{18}$–10^{26} m^{-3}) is the formation of particulates, which come from the explosive ejection of target material and, unfortunately, degrade coating smoothness. Arc filtering is the common solution to suppress particulate mixing in the deposition flux incident on substrates (Anders 1997, Robertson 2002). The very high ionization degrees in HiPIMS and vacuum arc make the manipulation of ion fluxes feasible with the correct configuration of external electric and magnetic fields (figure 3). A side effect of almost full ionized plasmas is the conformal coating of micro/nanostructured surfaces (Sarakinos *et al* 2010).

Carbon nanotubes (Garcia-Cespedes *et al* 2007) and graphene layers (Vijayaraghavan *et al* 2016) have been obtained by pulsed-DC chemical and physical vapour deposition, respectively. However, as in continuous DC plasma synthesis, the growth process requires substrate conditioning by increasing its temperature and depositing catalytic seeds at surface level. Nanocrystalline particles with low size dispersion have been generated in volume by dusty RF-plasmas both in continuous wave and in pulsed modulation. Acetylene (Berndt *et al* 2009) and silane (Boufendi and Bouchoule 1994) have been used for carbon and silicon nanoparticle formation, respectively. Pulsing the RF discharges contributed to control the nanocrystal size, and to activate-reactivate the growth near a critical frequency. Metallic nanoparticles were also generated by means of a highly ionized pulsed plasma recipe (Pilch *et al* 2013). However, the high plasma densities and temperatures suitable for the in-volume, high-yield synthesis of extended 1D and 2D nanostructures require the thermal ablation of solid anodes by arc plasma, i.e. atmospheric anodic arc discharges.

2.2. In-volume production by thermal plasma—atmospheric arcs

Anodic arc discharge consists of thermal erosion of anode material due to the incident electron current and the high gas temperature achieved, usually over 5000 K. Optical emission from arc plasmas actually consists of characteristic spectral lines superposed to a continuum thermal background (Williamson and DeJoseph 2003, Corbella *et al* 2021). Conditions near thermodynamic equilibrium are locally achieved in the core of the arc discharge, i.e. all species show similar temperatures. Hence, a flux of ablated species expands from the arc column and may coagulate and aggregate in nanomaterial form in the colder vicinity of the anode (non-equilibrium plasma). In-volume nucleation and synthesis are possible here because, in contrast to vacuum conditions, mean free path of plasma species is much smaller than characteristic reactor size. Finally, nanoparticles, formed from highly collisional processes, are transported through the arc chamber atmosphere to the walls preferentially by convection (Kundrapu and Keidar 2012, Shashurin and Keidar 2015, Keidar and Beilis 2018). Another nanosynthesis method based on thermal plasma is constituted by RF-driven inductive plasma torches, which is a well established plasma technology for the industrial production of nanopowder and nanostructured particles showing high purity and sphericity (Guo *et al* 2010, Mostaghimi and Boulos 2015).

The particular case of nanosynthesis by pulsed atmospheric arc has not been much explored as in low-pressure

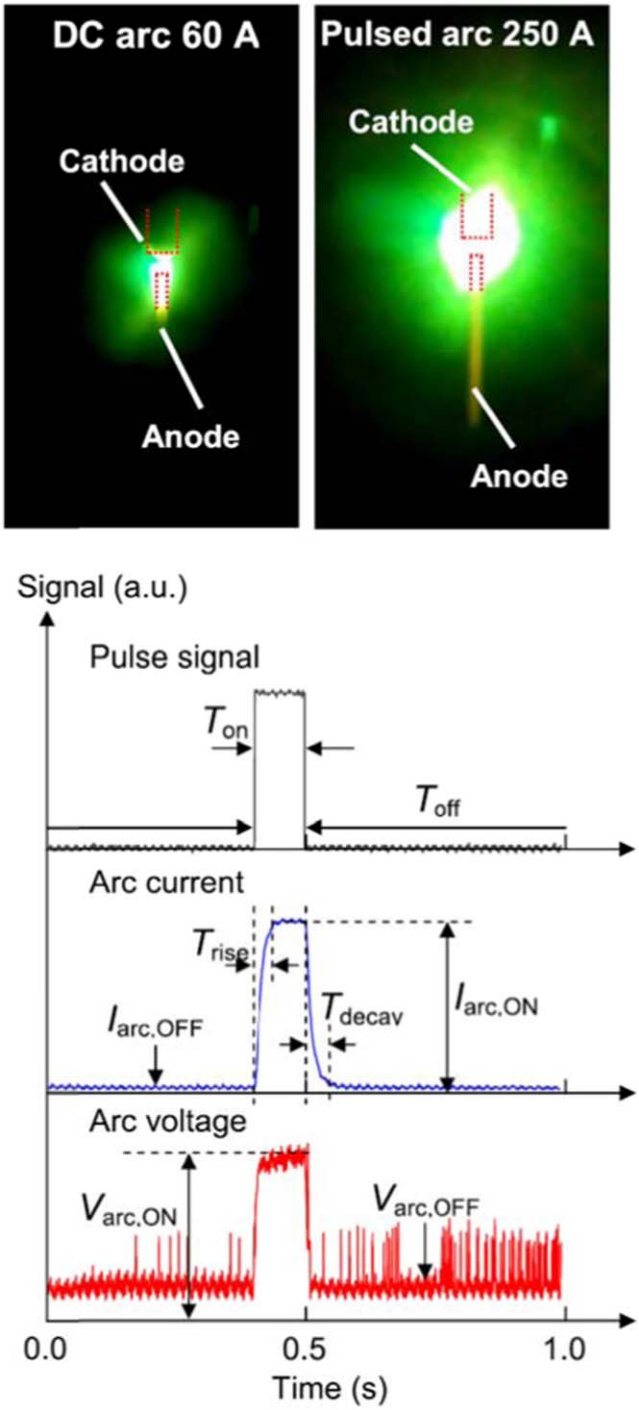

Figure 4. Top: Images of DC arc (60 A) and active phase of pulsed arc (2 Hz, 10% duty cycle, 250 A peak current) between graphite electrodes. The red dotted lines indicate the positions of the electrode edges. Bottom: periodical waveforms of set 1 Hz-pulse signals (10% duty cycle), arc current ($I_{arc,ON} \approx 250$ A), and arc voltage ($V_{arc,ON} \approx 50$ V). Reprinted from Corbella *et al* (2020a), with the permission of AIP Publishing.

pulsed discharges and needs more research. Atmospheric arc discharges deserve more attention due to their huge capabilities and relatively simple experimental setups (Sugai *et al* 1999b). Cleaner than wet chemistry reactions, none or less vacuum equipment is required in such arc processes, which can be deployed even in open air (Parkansky *et al* 2004, Fang *et al* 2012). Moreover, atmospheric arc technique shows a remarkable flexibility, as demonstrated in the review by Kim *et al* about arc discharges guided in the form of hot jets aimed to nanosynthesis (Kim and Kim 2019). Research on pulsed anodic arc discharge has been recently reactivated to support atmospheric arc synthesis of different nanomaterials (figure 4) (Corbella *et al* 2019c, Corbella *et al* 2019b). As discussed below, arcs undergoing periodical interruption and reignition show clear advantages in front of DC arcs concerning energy investment and nanostructure formation. This technique is basically motivated by the need of improving control over (1) discharge parameters and stability, and (2) nanoparticle size and structure. A more detailed analysis on pulsed arc nanosynthesis is discussed in the following sections.

3. Anodic arc nanosynthesis: a short overview

After having introduced the plasma methods more commonly employed in nanotechnology, here the focus is shifted to the present status in the fabrication of nanomaterials by means of atmospheric arc discharge from anode ablation process. The objectives of this section include outlining the different efforts in modelling, experimental progresses in atmospheric arc nanosynthesis, and the main issues that must be overcome.

3.1. Evolution of arc discharge modelling

Growth of nanoparticles in atmospheric arc plasmas starts from simultaneous sublimation of anode material and of catalyst powder. Carbon nanoparticle growth constitutes the most studied case. After combination of carbon and catalyst atoms and their ions within the vapor, nanoparticles are formed and deposited onto the cathode and chamber walls in an isobaric process. Hence, highly crystalline carbon nanostructures grown on catalyst seeds can be collected on a dedicated substrate (Keidar and Beilis 2018). Recent efforts have addressed the theory of nanoparticle nucleation stage in a cooling gas (Tacu *et al* 2020). Length and diameter of single wall carbon nanotubes (SWCNT) is shown to be controlled by catalyst diameter and plasma density that, in turn, is controlled by a magnetic field. In fact, it was demonstrated that an external magnetic field has a strong effect on length of a SWCNT (Keidar *et al* 2008). Numerical simulation techniques have been crucial to better understand the influence of experimental parameters on the nanoparticle growth kinetics (Kundrapu and Keidar 2012). The following subsections outline the basic approaches developed on nanoparticle growth modelling using 0D, 1D, and 2D models.

3.1.1. 0D (global) and 1D models. Some of the main physical phenomena relevant to nanoparticle synthesis in arc discharge can be described by constructing a global (integral) model of discharge plasma and electrodes as shown schematically in figure 5 (Keidar and Beilis 2009). The main features of the model are coupling between the interelectrode plasma and

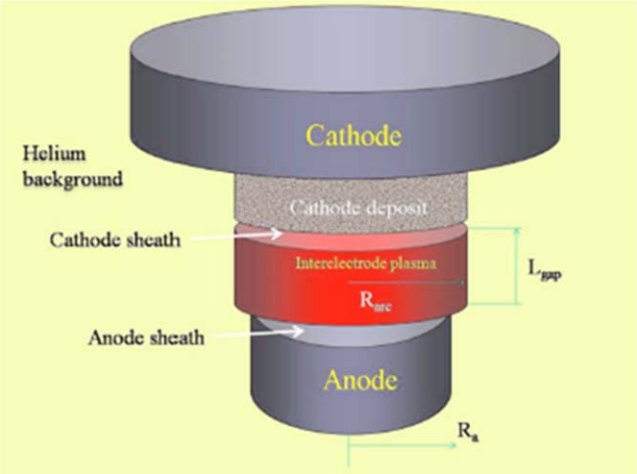

Figure 5. Schematic representation of the discharge plasma and electrodes considered for the global model of anodic arc discharge. Reprinted from Keidar and Beilis (2009), with the permission of AIP Publishing.

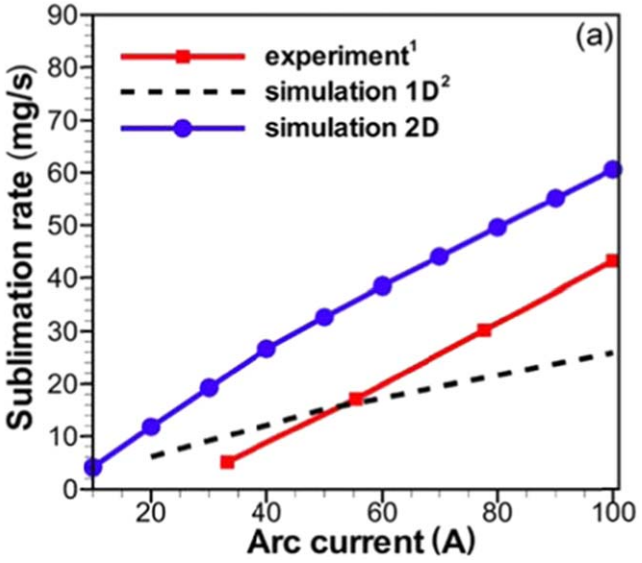

Figure 6. Sublimation characteristics corresponding to 2D simulation results, 1D/global simulations (Keidar and Beilis 2009), and experiments (Shashurin *et al* 2008). Helium background is maintained at around 500 Torr. Reprinted from Kundrapu and Keidar (2012), with the permission of AIP Publishing.

electrodes, current continuity at the electrodes, thermal regime of the electrodes, and the anode erosion rate.

During the arcing period, carbon species (or any other precursors) are supplied by anode erosion, which is determined by the anode temperature. In turn, anode temperature is affected by the heat flux from the interelectrode plasma, which is controlled by the pressure of the ablated species. On the other hand, the experiment indicates that erosion of the cathode is negligible during the arcing (Waldorff *et al* 2004). Ablated species expand and interact with background gas at or near atmospheric pressure condition. The dynamic boundary of the arc (the arc radius) is therefore determined by the interaction of carbon vapor with the helium background. Continuity of the current at the cathode implies that part of the current can be conducted by electrons emitted from the cathode, so that the total arc current at the cathode consists of ion and electron current. To that end, balance of energy at the cathode is determined by heat flux from the interelectrode plasma and by the heat losses due to radiation and heat conduction. Anode erosion is typically calculated based on Langmuir model (Langmuir 1913).

It is important to note that the cathode is in direct contact with arc plasma only during the initial stage of the discharge. During the continuous arcing, after about 30 s, part of the anode material is deposited on the cathode and forms a cathode deposit. This deposit material shows a porous carbon structure with properties that depend on the arc parameters (Keidar and Waas 2004, Lv *et al* 2005). Thus, during the continuous arcing, the cathode deposit is in contact with arc plasma, thereby protecting the cathode from erosion. Therefore, pulsed arcs will probably exhibit different behaviour in part due to absence of significant cathode deposition.

Interestingly, a non-monotonic dependence of arc discharge parameters on the arc current was experimentally observed. Such dependence can only be reproduced by this model by considering arc radius increase with arc current. Thus, more detailed multi-dimensional model is required for more accurate arc discharge simulation (Momeni *et al* 2020). Mansour and Hara have developed a 1D fluid model to explain the regimes of low and high ablation rates (Mansour and Hara 2019). Correlations between the discharge ablation mode and anode radius and current are discussed without considering the constraint of local thermodynamic equilibrium. As a consequence, radiative heat flux might play a relevant role in the plasma properties.

3.1.2. 2D models. A 2D model numerical simulation of carbon arc discharge was carried by Kundrapu and Keidar using a computational fluid dynamics (CFD) model for cylindrical coordinates (Kundrapu and Keidar 2012). Electrode heating and sublimation rate were coupled with flow expansion to evaluate the instantaneous mass rate of ablation self-consistently. Two-dimensional electric field is considered to simulate the arc. Conservative form of Navier–Stokes equations with electromagnetic source and energy equations are solved using SIMPLER algorithm (Patankar 1980). For a given arc current and electrode gap, the self-consistently obtained data such as density distribution of individual species, temperature distribution, and electric potential serve as inputs for the nanoparticle growth model. Species diffusion is solved separately for C, Ni, and Y, and ions, to obtain the respective mass fractions inside the fluid domain. The iterative calculation of density distribution is repeated until convergence is achieved at any time step. This procedure is repeated at all time steps to obtain the transient results.

Sublimation rates are obtained for current varying from 10 to 100 A, and are compared with those from experiments (Shashurin *et al* 2008) and one-dimensional/global model (Keidar and Beilis 2009). The comparison is shown in

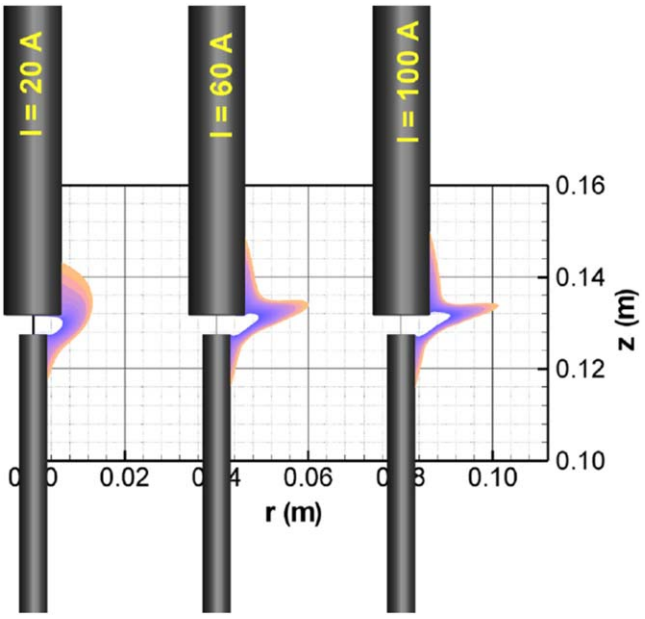

Figure 7. Regions of nanoparticle growth computed at different arc current values according to the numerical simulations of the 2D model by Kundrapu and Keidar. The size of the growth region decreases as arc current increases. Reprinted from Kundrapu and Keidar (2012), with the permission of AIP Publishing.

figure 6. The present 2D model predicts slightly higher sublimation rate compared to the experiments while maintaining the similar trend of variation. Though the 1D model showed better agreement for current $I < 60$ A, it could not capture the trend. The higher ablation rate is due to Langmuir evaporation model that considers vapor expands into vacuum. Finally, figure 7 shows the resulting nanoparticle growth zones after this 2D model.

The 2D model solves transient equations with an instantaneous solver for potential field. By varying the pulse currents corresponding to the given voltage signal, the model could be extended to simulate pulsed arcs.

Chen *et al* considered a mechanism of anode spot formation (Chen *et al* 2020). It was concluded that the spot formation is not related to plasma instability, as commonly believed in case of constricted discharge columns, but rather occurs due to the highly nonlinear nature of heat balance in the anode. Simulation results also show that the arc can reach local chemical equilibrium (LCE) state in the column region while the local thermal equilibrium (LTE) state is not typically achieved for experimental conditions. The model shows the relevance of accounting for different temperatures, one for the electrons and another one for the gas, in the modelling of short carbon arcs. Such a model constitutes a valuable update to the standard picture of anodic arc ablation physics, and it should be considered for an upgrade to the pulsed arc scheme.

3.2. Accomplishments and challenges

Arc discharge near atmospheric pressure is useful to investigate the growth of nano- and microscopic objects from a fundamental approach. In fact, the control of basic variables, like discharge voltage and electrode geometries, makes this technique very adequate to gain understanding on nanosynthesis physics and to transfer deposition recipes from pilot reactors to industrial plants.

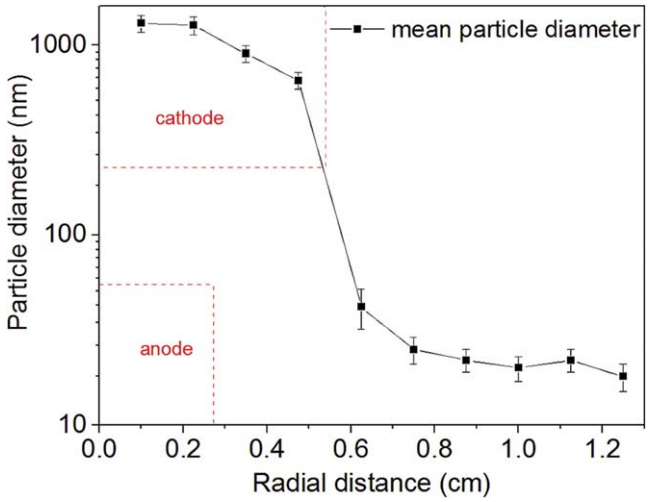

Figure 8. Plot showing carbon particle diameter calculated from LII measurements at different radial positions from the interelectrode axis. Reprinted from Yatom *et al* (2017a), © 2017 Elsevier Ltd. All rights reserved.

After the milestone of CNT fabrication by arc method (Iijima 1991), nanosynthesis field evolved rapidly and a better control on nanoparticle production has been achieved thanks to modelling tools and plasma diagnostics. For instance, laser diagnostics have been intensively used to map the main growth zones of carbon nanoparticles, which constitute the core of nanomaterials like fullerenes, nanotubes and graphene (Vekselman *et al* 2017, Yatom *et al* 2018). Yatom *et al* found mean particle sizes on the arc region spanning from around 1 μm down to 20 nm along a radial distance of 1 cm, as calculated from laser-induced incandescence diagnostics (LII) (figure 8) (Yatom *et al* 2017a). Further studies using time-resolved LII provided 2D mappings of nanocarbon growth regions near the arc zone, which matched roughly with profiles computed in earlier works (figure 7) (Yatom *et al* 2018, Kundrapu and Keidar 2012). Fast electrostatic probes were very helpful to explore correlations between discharge parameters and the formation of arc spots (Shashurin *et al* 2011). On the other hand, growth models of CNTs (Keidar and Waas 2004) suggested the input of magnetic forces in the arc regions to enhance and stabilize CNT formation (Anazawa *et al* 2002, Volotskova *et al* 2010). Influence of magnetic fields on nanotube growth and gas temperature was studied by optical emission spectroscopy focused on different arc regions (Li *et al* 2012). AC gliding arc plasma, a transition arc technique widely used for gas treatment, was recently employed to generate carbon nanostructures via precursor dissociation and electrode exfoliation (Tu and Whitehead 2014, Ma *et al* 2021).

Nanomaterials with compositions other than carbon-based have also constituted a focus of active research. BNNT were originally synthesized by arc-ablating a pressed rod of

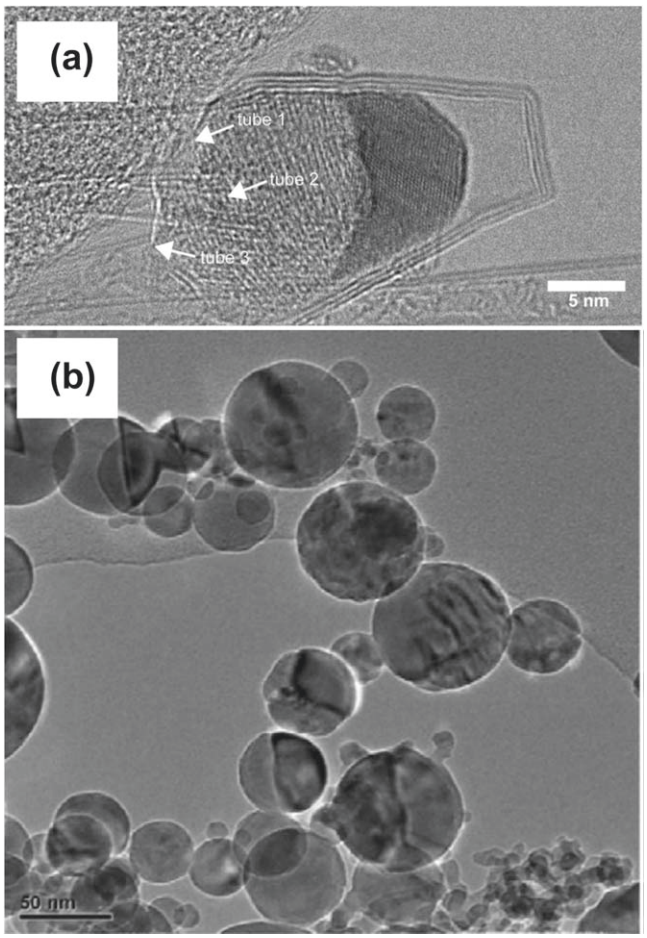

Figure 9. (a) HRTEM image of boron nitride nanotubes (BNNTs) obtained from DC arc discharge of a boron-rich anode in nitrogen atmosphere. Three BNNTs are grown from a boron nanoparticle expelled from the anode. Reproduced from Yeh *et al* (2017). CC BY 4.0. (b) TEM image of TiO_2 nanoparticles synthesized by means of DC arc discharge of a Ti anode in air atmosphere at 300 Torr. Reproduced from Fang *et al* (2012), Copyright © 2011 Elsevier B.V. All rights reserved.

h-BN inserted into a hollow tungsten anode (Chopra *et al* 1995). More recently, such boron nanostructures were produced by DC-arcing on a boron anode facing a Cu cathode in a reactive atmosphere of nitrogen. Metal inserts were used on the boron ingot to increase its electrical conductivity. The HRTEM image in figure 9(a) shows a few BNNTs apparently seeded on a precursor boron nanoparticle (Yeh *et al* 2017). The subject of early stages of BNNT growth has been addressed by *ab initio* simulations combined with experiments (Santra *et al* 2018). Significant progress on modelling of BNNT formation is provided by integrated kinetic and thermodynamic approaches (Barsukov *et al* 2021). Actually, strong component in plasma chemistry must be considered when addressing B/N_2 gas mixtures. Fullerenes of MoS_2 showing core–shell structure (2–3 layers, 5–15 nm) were synthesized under water from arcs using Mo hollow anodes with packed MoS_2 powder. (Sano *et al* 2003, Alexandrou *et al* 2003) TiO_2 nanoparticles, which are widely used to modify surface and optical properties, have been obtained by eroding a Ti anode in air atmosphere at 300 Torr (Fang *et al* 2012). The TiO_2 nanostructures are predominantly spherical and crystalline particles. (figure 9(b)). Wide size distributions (from nm to μm) of magnetite powders with high tunnelling magnetoresistance were deposited from arc of Fe rod in a partial oxygen atmosphere (Prakash *et al* 2016). The unintentional production of different iron oxide phases modified the magnetic properties of the samples.

The above advances outline the forefront in arc performance to create nanomaterials. However, despite the versatility of atmospheric arc technique, several issues which can affect process control and repeatability have been detected. Above all, instability in arc discharges is a common issue that must be thoroughly addressed to ensure the production of high-quality nanomaterials. This and other aspects that follow have been remarked and should be considered to prepare well-defined arc discharge experiments near atmospheric pressure:

- *Stability:* Main concern is related to uncontrolled interaction between arc glow and electrodes (Liang *et al* 2017). Instabilities in carbon discharges, detectable as oscillations in arc voltage and optical emission, have been related to the particular geometries of ablating anode (Gershman and Raitses 2016, Yatom *et al* 2017b). Even submerged arcs show instable behaviour. (Sano *et al* 2003, Bhattacharya *et al* 2019, Hernandez-Tabares *et al* 2021). Changes in anode tip geometry in continuous DC arcs are a known problem and are correlated with instability formation (Ushio 1988). Thus, a better control on tip shape could contribute to arc stabilization.
- *Purity:* Anodic carbon arcs deliver nanomaterials mixed with larger particulates (He *et al* 2007). Soot production needs to be suppressed or minimized if one strives for maximal purity of arc products. Such improvement is possible by determining the dominant material produced at different arc stages (Sugai *et al* 2000). Formation of atomic species, nanoparticles and aggregates need to be tracked during whole arc process (Corbella *et al* 2019c).
- *Compound nanomaterials:* Precursor fidelity is an important concern related to synthesis of alloy nanoparticles. Chemical compositions of product and precursor materials do not necessarily match. In consequence, strategies to control the stoichiometry of product nanomaterials, which are beyond adding reactive gases (Prakash *et al* 2016, Yeh *et al* 2017) and working in liquid media (Kim *et al* 2021), are in high demand nowadays.
- *Process flexibility:* A better control over nanomaterial size and structure can be achieved by additional discharge parameters. Pulsed arcs can upgrade DC processes by adding arc repetition rate, pulse width and peak power values (Sugai *et al* 2000, Corbella *et al* 2020a). Moreover, the freedom of pulsing an arc discharge enables estimation of basic plasma parameters by simple electric measurements (Corbella *et al* 2019a). Accurate positioning of the arc synthesis region is not straightforward. In fact, nanoparticle motion is restricted to convection flow lines (Kundrapu and Keidar 2012). Thus, a strategy to

steer deposition location is needed (Parkansky *et al* 2004).

- *Environmental compatibility:* When arc nanosynthesis takes place in liquids, arc processes must be performed with lower thermal loads (Sano *et al* 2003). Here, all aggregation phases are engaged: a plasma is developed within a liquid matrix to generate solid particles surrounded by gas phase (Kim *et al* 2021). This scenario demands steady balance among all phases to avoid excessive formation of high-pressure bubbles. Pulsed arc discharges are an elegant route to attain stable plasmas in liquid (Omurzak *et al* 2007).
- *Economy:* Development of arc processes involving rational power consumption is priority, especially in view of upscaling for industrial implementation. Pulsed anodic arcs constitute a route to minimize energy investment in nanosynthesis (Corbella *et al* 2020b). Re-triggering after electrode separation requires very high voltages (1 kV) for gas breakdown. (Sugai *et al* 2000) Much lower voltages (20–40 V) can be involved via intermittent contacting of anode and cathode, (Imasaka *et al* 2006) and by designing voltage waveforms that keep the arc discharge latent during inactive pulse period (Corbella *et al* 2019c).

The above list of limitations justifies scenarios where pulsed power implementation would be advantageous for programming advanced recipes of arc discharges aimed to nanoproducts with optimal properties. The following section discusses up-to-date strategies utilized to deposit nanomaterials using pulsed arc power.

4. Implementing pulsed power in arc discharges for nanosynthesis

This section intends to classify the diverse approaches made in pulsed arc production by addressing the challenges listed above. Therefore, the discussion has been articulated from the perspective of four main points: (1) understanding growth mechanisms and improving quality of carbon nanostructures, (2) positioning arc source for localized deposition of nanomaterials, (3) increasing material choice and minimizing power consumption by pulsed arcs in liquid phase, and (4) improving synthesis parameters for more stable and efficient production by modelling and advanced diagnostics.

4.1. Fine-tuning the structure of carbon nanomaterials

Sugai *et al* produced fullerenes (Sugai *et al* 1999b) and single-walled carbon nanotubes (SWCNT) (Sugai *et al* 1999a) by means of high-temperature arc discharge. The experimental setup consisted of a reaction vessel inside a furnace, in which two facing graphite electrodes and a cooled-down substrate holder were installed. Ni/Co composite graphite electrode was used to grow SWCNT. The deposition chamber design is relatively simple and, given its flexibility of manipulation, it has inspired other groups (figure 10)

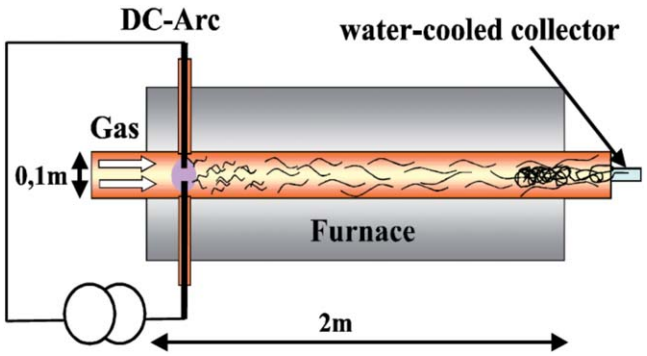

Figure 10. Typical configuration in high-temperature pulsed arc nanosynthesis with water trap collector. A high voltage stage (ca. 1 kV) of ignition is followed by low voltage (ca. 50 V) steady arc stage. The anode consists of graphite with additions of transition metal oxide for catalysis purposes. Reproduced from Roch *et al* (2007), John Wiley & Sons. Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

(Roch *et al* 2007). Hence, the generated species in the arc underwent annealing conditions (1000 °C in 500 Torr He, Ar, or Kr) while transported through the vessel to the substrate. Pulsed high voltages of 1.1 kV were used for arc ignition in the electrode gap. Pulse frequencies between 3 and 300 Hz with 1% duty cycle were performed. The concentration of the obtained C_{60} increased with the pulse duration from 50 μs to 3 ms. Interestingly, when using catalyst-doped graphite electrode, SWCNT production showed similar trend with pulse width as well, but it inhibited fullerene growth.

Experiments with the furnace reactor design from figure 10 had been performed previously to study formation mechanism of nanocarbons. The trials revealed a competitive process between fullerene and SWCNT synthesis (Sugai *et al* 2000). The participation of catalysts and the discharge duration determined the dominant nanoparticle deposited onto the substrate. Catalyst was introduced by using metal-doped (Ni/Co and Ni/Y) composite graphite electrodes. By extending the pulsed width up to almost 1 s, Sugai *et al* found that the pulsed arc regime transitioned to a steady arc regime at a pulse duration of 3 ms. The exploration of long pulse times was feasible by combining the igniting high voltages (1.1 kV) with lower voltage operation for the steady DC arc (40 V). The production of SWCNT became dominant in stronger annealing conditions partially due to major graphite fragmentation. In addition, Sugai *et al* found that 1200 °C was a critical temperature for the synthesis of double-walled CNT (DWCNT) (Sugai *et al* 2003) figure 11 shows TEM images and Raman spectra of the produced samples. Raman peaks 214 and 136 cm^{-1}, corresponding to specific inner and outer DWCNT diameters, are enhanced at higher temperatures. The mixture of different nanotubes was purified by oxidation in air, and the resulting samples presented inner and outer diameters, very well defined by TEM analysis, compatible with the sizes of DWCNT. This technique enabled the production of high-quality carbon nanomaterials suitable for nano-electronic devices thanks to the controllable transport properties (Shimada *et al* 2004) and an optimized synthesis and

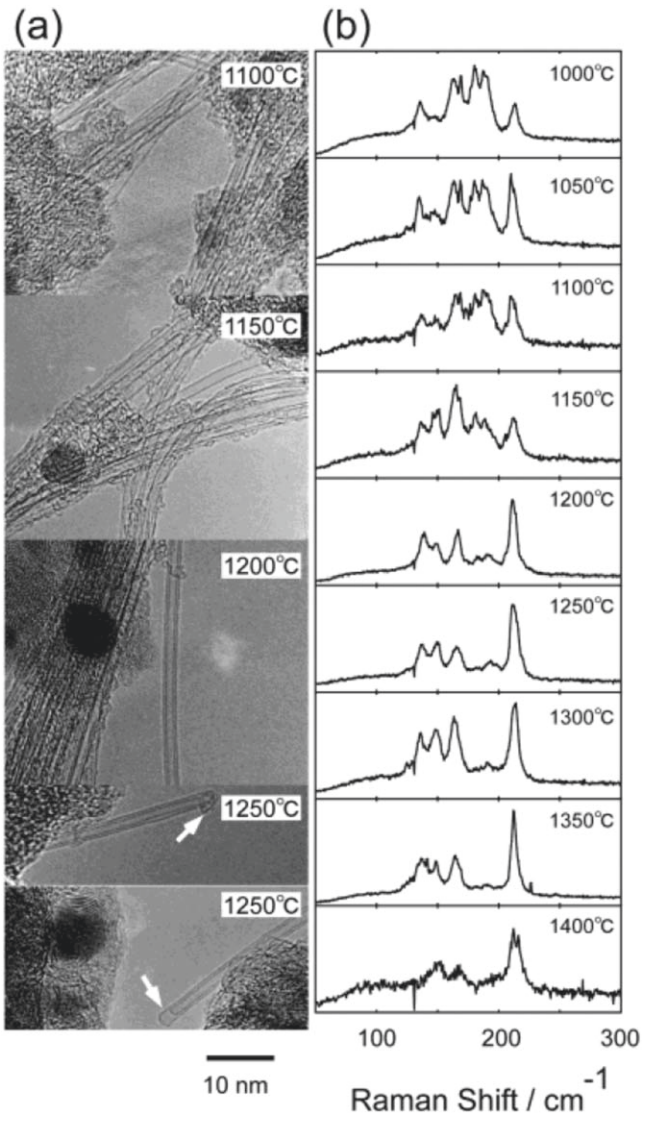

Figure 11. (a) TEM images and (b) corresponding Raman spectra of carbon nanotubes synthesized by pulsed arc discharge using a furnace reactor at different temperatures. The formation of DWCNT is activated beyond 1200 °C. This statement is supported by the doubly capped structures observed at the end of the nanotubes (indicated with arrows). Reprinted with permission from Sugai *et al* (2003). Copyright © 2003, American Chemical Society.

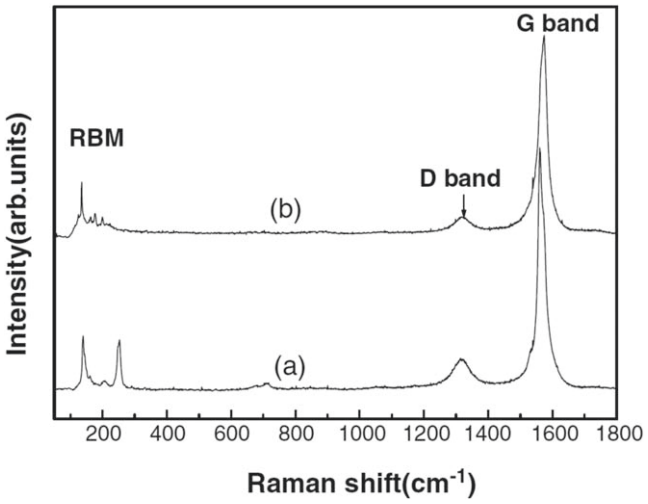

Figure 12. Raman spectra of SWCNT prepared by pulsed carbon arc in (a) air and (b) He atmospheres. Radial breathing modes (RBM), indicative of CNTs, are more pronounced when arcing in air. Reprinted from Li *et al* (2008), Copyright © 2008 Elsevier Ltd. All rights reserved.

post-treatment method able to provide DWCNT with purity of at least 95% (Yoshida *et al* 2008).

By using the furnace setup above, Roch *et al* (2007) discussed the advantages presented by the pulsed arc production of SWCNT and compared results with laser vaporization. The investigation showed similar size distributions and yield productions in both pulsed arc and laser ablation techniques, thereby suggesting similar growth mechanisms of carbon nanomaterials. Li *et al* (2008) proved with this reactor configuration that, after a pre-heating of catalyst in vacuum, high-quality SWCNT could be synthesized in air at reduced pressure. Figure 12 compares the Raman spectra of samples deposited in air and He atmospheres. The marked presence of two peaks in radial breathing modes (RBM) region indicates a more uniform diameter distribution in the case of air environment.

Muhl *et al* (2003) produced carbon films by energizing with pulsed high-current two separated rods, working as arc electrodes, near a substrate. After showing that this method proved efficient to deposit sp^2-rich amorphous carbon films, the setup was used to produce carbon and carbon-encapsulated metal nanoparticles by tuning conveniently the arc discharge pressure (Muhl *et al* 2005). The experiments were performed using 40 ms-pulses with peak currents of around 1000 A in atmospheres of air, He, and Ar at pressures from 0.05 up to 500 Torr. In another sophisticated instrument, Kia *et al* conducted arc discharge growth of multi-walled carbon nanotubes (MWCNT) and carbon nano-onions by applying a special configuration of axial electric field and orthogonal magnetic field on an arc plasma generated between a needle anode and a bowl-shaped cathode (Kia and Bonabi 2012). Pulse frequencies from 50 to 400 Hz and a pulse width of 0.3 μs were used to control the grown nanostructures.

4.2. Nanofabrication with spatial resolution

Arc deposition systems need to be upgraded to enable local nanofabrication in specific positions after the synthesis parameters have been optimized and the nanostructured materials show competitive physical-chemical properties. Although very high writing resolutions like in nanolithography or scanning probe microscopy cannot be achieved by arc discharges, micro-resolved positioning is feasible with adequate electromechanical system (figure 13) (Tsai *et al* 2009).

Parkansky *et al* (1998) constructed a setup based on a local discharge positioning system using an oscillatory anode that scanned the substrate area in open air. This instrument was originally conceived for deposition of WC-based hard alloy coatings. It was also used to study energy balance in anodic arc erosion of metals (Parkansky *et al* 1993).

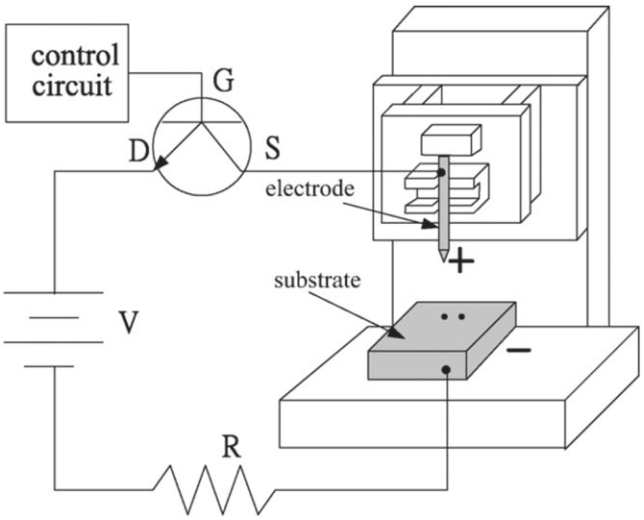

Figure 13. Sketch of a micro electro-discharge system aimed to produce carbon nanotubes by single pulse arc discharge in air. Reprinted from Tsai *et al* (2009), Copyright © 2008 Elsevier B.V. All rights reserved.

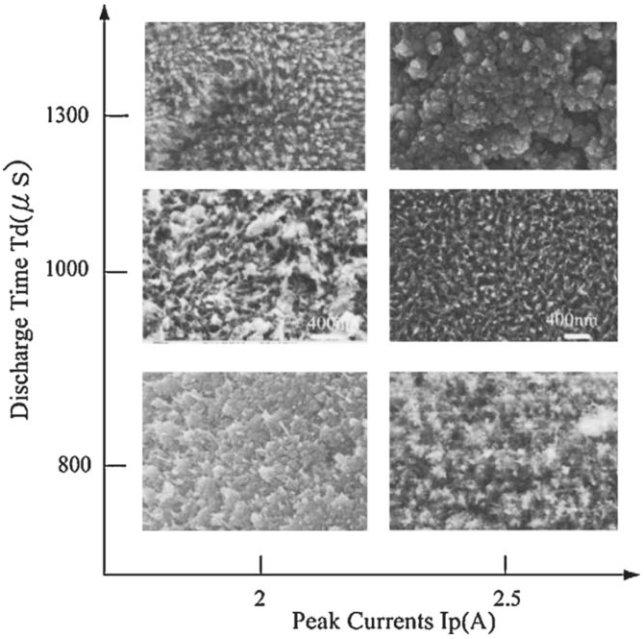

Figure 14. TEM images showing the morphology of carbon nanostructures obtained at different discharge times and peak currents in the pulsed arc experiments in air. Needle-like structures start appearing at 2 A after 1000 μs of discharge time. Reprinted from Tsai *et al* (2009), Copyright © 2008 Elsevier B.V. All rights reserved.

Subsequently, the application scope was expanded to carbon nanotube growth. Thin graphite bars were used as cathode, while movable substrate holders (graphite, Ni, or Cu surfaces) acted as anode. MWCNTs up to 3 μm in length were deposited at selected positions using single-pulse arcs in open air at current amplitudes 7–100 A (Parkansky *et al* 2004). Pulse width was comprised between 0.2 and 26 μs for the emitted single or few pulsed arcs (100 Hz). The substrate, which was not intentionally heated, was moved in steps of

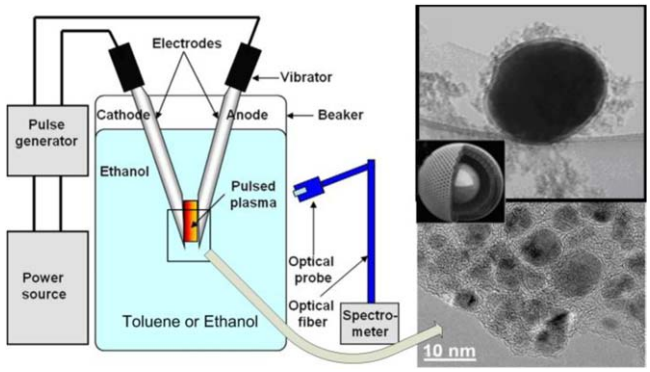

Figure 15. Sketch illustrating the pulsed plasma in liquid method together with TEM micrographs showing the Fe nanoparticles fabricated with this technique. Reproduced from Omurzak *et al* (2018). © IOP Publishing Ltd. CC BY 3.0.

0.01 mm between successive arc pulses. Low or high voltage arcs were applied when working in intermittent contact or non-contact modes, respectively, leaving affected areas of a few hundred nm^2. This technique is very promising for the fabrication of nano-electronic devices and biological probes. Similar pulsed arc treatments were also used to texture steel surfaces for tribological applications (Moshkovith *et al* 2007).

Tsai *et al* (2008) developed the oscillatory electrode concept by constructing an electromechanical discharge machine, in which single discharges in open air yielded samples of carbon nanotubes in an accurate and reproducible process. Both sample holder and graphite rod, which were set 1–2 μm apart, could be displaced to enable programmed depositions of nanotube arrays. Nanotubes were formed at a minimal current threshold of 2 A and 1 s of pulse length (figure 14) (Tsai *et al* 2009). More energetic pulses, either by higher current or longer pulses, yielded oxidized nanotubes due to the operation under ambient conditions. Thus, adequate discharge parameters were maintained near the threshold values to prevent sample oxidation.

4.3. Nanoparticle growth by plasma in liquid phase

Liquid phase arc plasmas are not strictly considered as atmospheric arcs, but their versatility justifies a short overview on this topic. Namely, liquid phase plasma processes address three issues: (1) develop cost-effective processes because use of gases and vacuum equipment are avoided; (2) high thermal loads can be prevented by surrounding liquid, and (3) chemical precursors can be provided in solution form (Kim *et al* (2021)). A prominent downside is the limitation to operate at average powers low enough to prevent from complete liquid evaporation and to limit quenching zone of evaporated anode (Sano *et al* 2003). Pulsed arc plasmas are ideal for nanofabrication in liquids since an intermittent power input prevents from major heating of the deposition vessel and related problems, like arc instabilities due to rapid changes in electrode gap and anode tip.

Parkansky *et al* (2004) adapted their pulsed arc system to be operated in ethanol for the synthesis of micro- and nanoparticles. Their composition was determined by carbon from

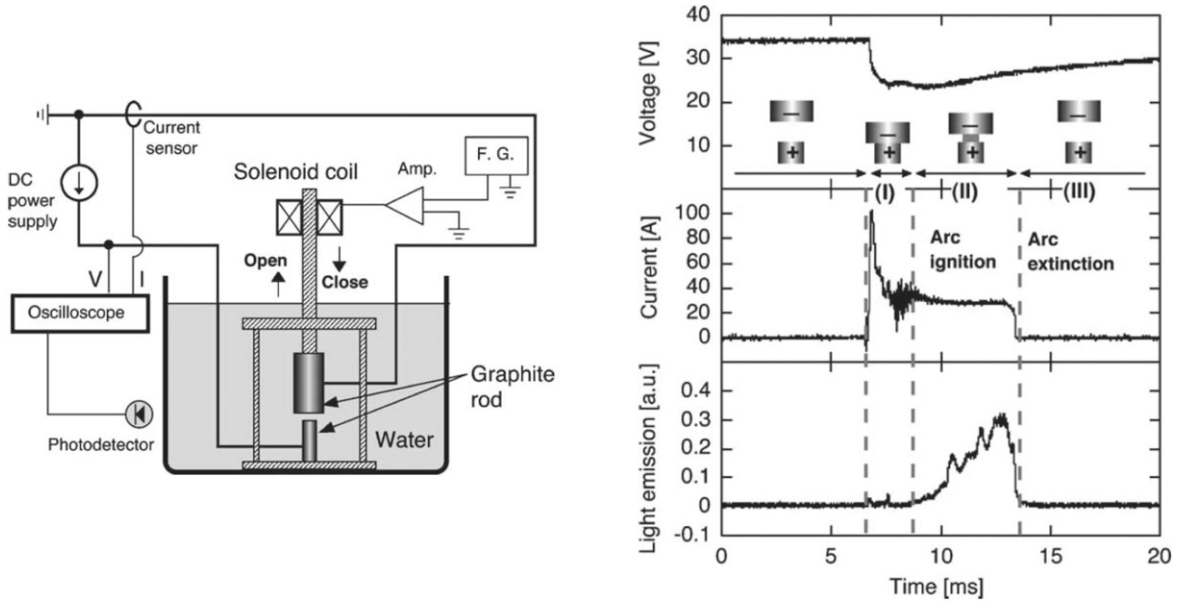

Figure 16. Left: scheme of an intermittent arc discharge experiment with the electrodes submerged in water to synthesize carbon nanostructures. Right: typical waveforms measured in arc voltage, arc current and light emission during pulsed arc discharge in water. Reprinted from Imasaka *et al* (2006), Copyright © 2005 Elsevier B.V. All rights reserved.

the ethanol solution and selecting adequate electrode material, whereas sizes could be tuned by means of discharge parameters (Parkansky *et al* 2005). Hence, W, Ni, and C nano-onions could be obtained (<20 nm), and core–shell Me@C particles were also fabricated (<25 μm). Omurzak *et al* designed an arc discharge cell lodging two contacting electrodes connected each one to a vibrator element. In this configuration, intermittent discharges were produced by supplying an AC signal (several 100 V and around 10 A at Hz–kHz range) to the electrode system, whose contact point was periodically readjusted in each cycle (figure 15) (Omurzak *et al* 2007). A plethora of multi-component metallic nanoparticles, some with core–shell structure, have been synthesized by combining different electrode materials, surfactant, and liquid composition. Examples of deposited nanoparticles, some presenting magnetic properties and aimed to biomedical applications: high-purity C_{60}, TiO and Cu; (Omurzak *et al* 2007) pure tetragonal ZrO_2; (Chen *et al* 2011) Co@C, Ni@C, and Fe@C; (Abdullaeva *et al* 2012) CoC_x@C, (Chen *et al* 2013) and pure α-Fe (Kelgenbaeva *et al* 2014).

Pootawang *et al* (2012) synthesized bimetallic Ag/Pt nanoparticles by applying pulsed arcs between metallic electrodes (gap: 0.5 mm) in a NaCl solution. High voltage pulses of 0.5 kV at 15 kHz of frequency and 3 μs duration were applied at different discharge times. A transition to nanocomposite structure was found after a discharge time of 30 s. Intermittent arc discharges in water were reported by Imasaka *et al* to produce carbon nano-onions and nanotubes (figure 16) (Imasaka *et al* 2006). A similar deposition method was employed by Takekoshi *et al* to produce metal-encapsulated carbon nanotubes (Takekoshi *et al* 2012). Imasaka *et al* applied arc currents of 30 A and arc voltages of 35 V to oscillating graphite electrodes submerged in water. Low voltage values were sufficient to generate the arcs thanks to the intermittent attaching-detaching conditions of the electrodes. The chopping of the supplied DC power by this periodical movement enabled the production of a pulsed arc discharge. Electrode motion was held at frequencies between 15 and 20 Hz for a few hours, and it resulted in the formation of carbon nanoparticles (nano-onions: 15–20 nm; MWCNT: 100–500 nm of length) and waveforms of discharge current and voltage shown in figure 16.

4.4. Nanosynthesis efficiency and stability

Stability of anodic arc discharge is crucial to secure the control and reproducibility of nanomaterial deposition processes. The nature of arc attachment to the electrodes determines process stability to a great extent (Liang *et al* 2017). Murooka *et al* explored short pulsed arc discharges as a resource to limit the migration of arc spots. In their setup, two aligned graphite electrodes (gap: 1–3 mm) were fed with 20 kHz pulses for a few seconds in Ar atmosphere at 250–500 Torr. The discharge current in the small cylindrical vessel was limited to 2 A. As a result, carbon nanoproducts were mostly assembled in the central part of the cathode surface, indicating a better control over arc spot motion (Murooka *et al* 2000, Murooka *et al* 2001).

Corbella *et al* investigated the arc discharge performance between vertically aligned graphite electrodes at 300 Torr in He. The discharge was sustained by either DC (35–65 V, 60–150 A) or pulsed power (50 V peak, 180–250 A peak), the latter operated at 1–5 Hz and 10% duty cycle (Corbella *et al* 2019c). Figure 4 shows typical discharge waveforms. A global model was used to interpret temporal evolution of gas pressure in the arc chamber (figure 17). Briefly, DC arc discharge underwent a 1 s-phase of pressure increase due to breakdown anode ablation, which was followed by a long

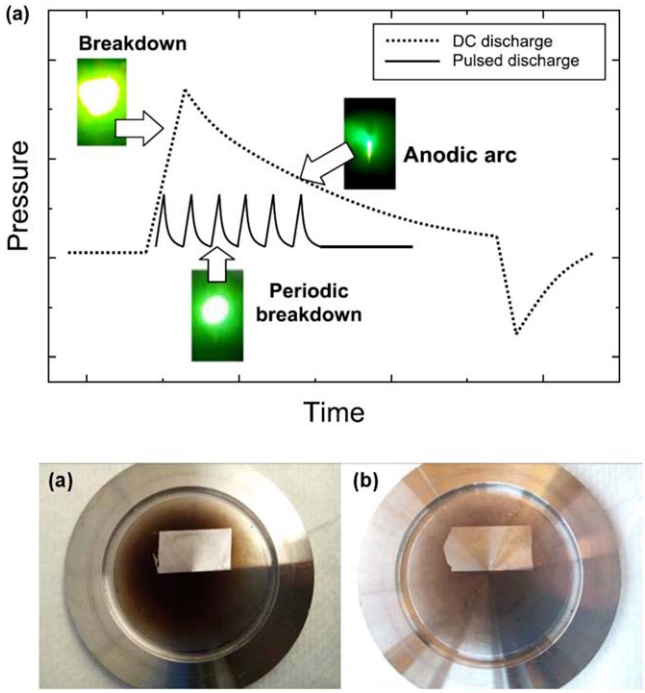

Figure 17. Top: temporal evolution model of gas pressure during DC (dotted line) and pulsed (solid line) arc discharges between graphite electrodes. Typical images of glowing arc on the ablating anode are inserted. Bottom: photos comparing blank flange surface after exposure to arc atmosphere excited with DC (left) and pulsed (right) energies. Pulsed arc discharge minimizes dust formation. Reproduced from (Corbella *et al* 2019c). © IOP Publishing Ltd. All rights reserved.

phase of monotonic pressure decrease attributed to formation of dust and macroparticles. In contrast, pulsed arc regime consisted of periodical breakdown-like phases, which never reached the dusty stage characteristic of continuous DC discharge. Pulsed carbon arc discharges show average ablation rates (≈1 mg s^{-1}) and powers (≈1 kW) competitive with values typical of DC discharges. Also, pulsed discharge operation provided more stable processes basically due to arc anchoring to the inter-electrode region.

Pulsed anodic arc discharges consist of short ON (active) and long OFF (inactive) phases. The nanoproducts deposited on the cathode surface were a mixture of carbon nanotubes and graphene nanoplatelet layers (Fang *et al* 2016, Fang *et al* 2019, Corbella *et al* 2019c). Electrical and optical diagnostics confirmed that the arc discharge was never extinguished during the OFF phase, but it kept striking in a weaker, constricted mode, until the start of next ON cycle (Corbella *et al* 2019a. To prevent arc extinction, the arc discharge voltage must float always at a minimal threshold value (20–30 V) determined by the voltage drops of the plasma sheaths. In order to study the growth mechanisms of carbon nanomaterials, growth rate during 1 Hz pulsed arc was tracked in spatial and temporal resolution using a fast movable probe (figure 18) (Corbella *et al* 2020c). The oscillating motion of the probe was set at the same frequency as the pulsed signal's one with a time delay. The selected delay in probe oscillation enabled collecting material from the arc region at different discharge phases with 10 ms of time exposure.

The deposition rate measured at the probe tip (5 mm from arc core) together with the corresponding arc current waveform are depicted in figure 19. Material growth is only associated with the ON phase (100 ms), whereas the deposited material during the OFF phase (900 ms) is negligible. Raman spectroscopy and SEM analysis showed that the collected material during ON times was rich in carbon nanostructures, and that arc at OFF times left traces of amorphous carbon (Corbella *et al* 2020c). Furthermore, Raman spectra of the deposited nanomaterial tracked along the probe shows that the ratio between G′ and G carbon bands decays significantly slower along the probe than the DC-associated ratio (figure 19). Since the G'/G intensity ratio is a measure of graphene nano-platelet concentration (Graf *et al* 2007, Ferrari and Basko 2013), it is concluded that carbon nanostructures reach longer distances than homologous DC processes (Corbella *et al* 2020b).

Similar experiments were conducted to study the pulsed arc synthesis of MoS_2 nanomaterials in He atmosphere in order to avoid use of sulphur reagent (Corbella *et al* 2019b). A graphite hollow anode densely packed with MoS_2 powder was ablated by means of 2 Hz-pulses having around 300 A of peak current. The evaporated material was deposited on a collecting probe placed in the vicinity of the electrode gap. The Raman spectra of the middle probe region shows two characteristic MoS_2 bands, $E^1_{2g} \approx 385$ cm^{-1} and $A_{1g} \approx 410$ cm^{-1}, whose separation is consistent with the formation of a few layers (3 to 5) of MoS_2 (Lee *et al* 2010, Mukherjee *et al* 2015). Flakes of around 1 nm in thickness were measured by AFM imaging, which supports the presence of elementary MoS_2 layers.

5. Summary and outlook

The present topical review constitutes an up-to-date report on the status of nanomaterial synthesis performed by pulsed anodic arcs in gas and liquid phases. The advantages provided by pulsed arcs and other concurrent plasma methods for nanomaterial synthesis have been discussed. Table 1 shows the main characteristics and limitations of the different pulsed plasma techniques used to deposit nanostructured materials. The advantages of operating high-pressure arc discharges in pulsed mode have led to many achievements, from addressing instability issues through improving arc control. Such milestones are classified in this article according to the intended research goal or application, namely: nanostructure tuning, local deposition, liquid phase plasma synthesis, and arc stabilization.

The main aspects addressed by pulsed arc methods for nanomaterial synthesis are summarized in table 2. First, formation mechanisms of carbon nanotubes and fullerenes in high-temperature environment have been unravelled by pulsing carbon arcs at different pulse widths. The dominant processes leading to one or another kind of nanoparticles were identified by tracking structure and morphologies of carbon deposits produced using pulse lengths from several

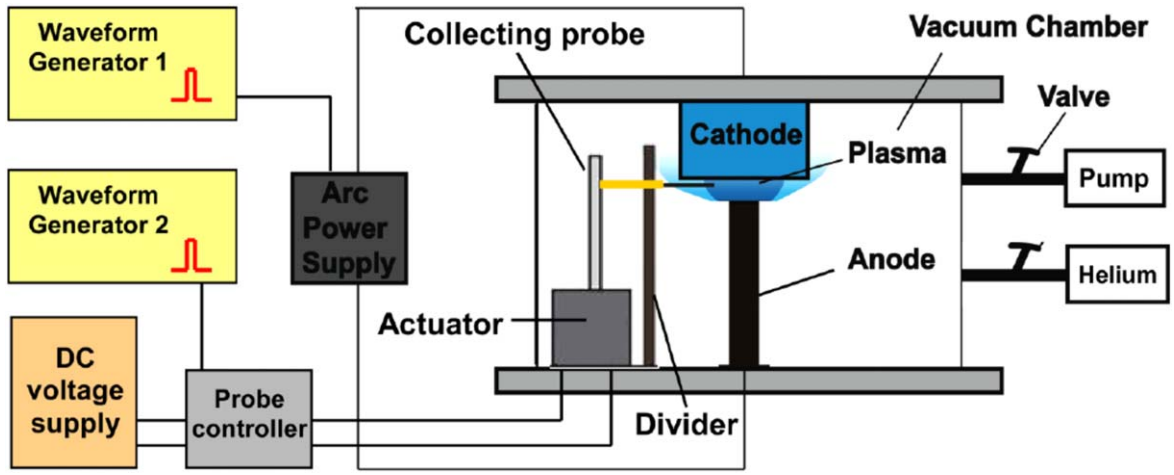

Figure 18. Scheme of the experimental setup of arc deposition equipped with the fast-collecting probe for time- and spatially resolved growth analyses. Reprinted from Corbella *et al* (2020c), with the permission of AIP Publishing.

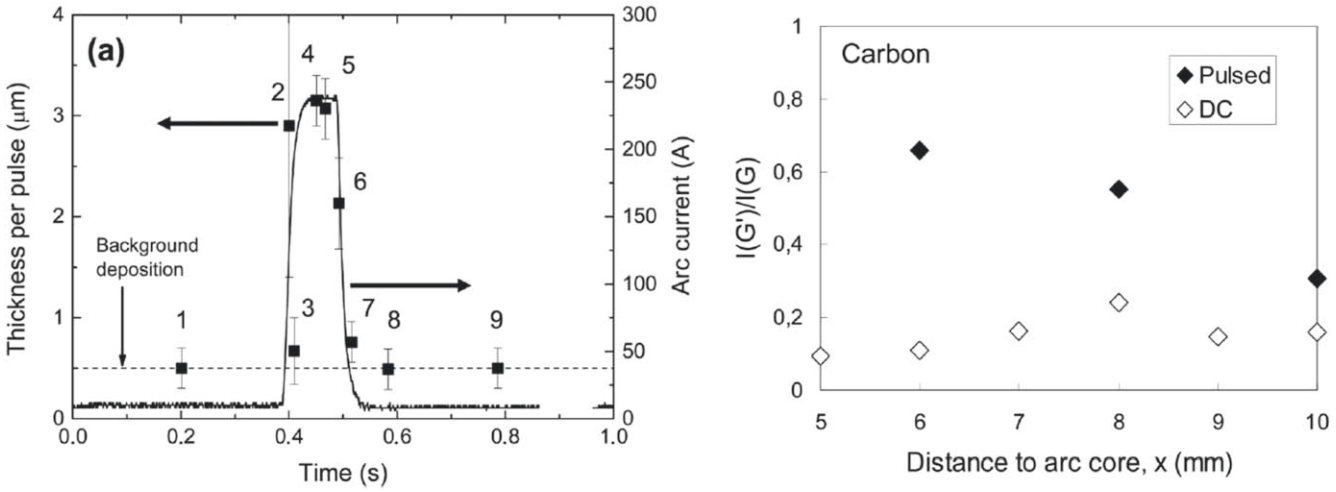

Figure 19. Left: tracking of carbon species deposition rate onto the fast probe along one pulse cycle (solid line: arc current waveform). Reprinted from Corbella *et al* (2020c), with the permission of AIP Publishing. Right: intensity ratio of the Raman G' and G peaks for fast probe experiments in DC mode, (Fang *et al* 2016) and pulsed mode (Corbella *et al* 2020b). The reach of carbon nanomaterials is longer in the case of pulsed arc operation. Reprinted from Corbella *et al* (2020b), with the permission of AIP Publishing.

microseconds to the second range. In second place, controlled confinement of single arc pulses enabled deposition of carbon nanomaterials in specific locations of a flat substrate. CNTs occupying zones of a few hundred nanometres could be generated with a spatial resolution of several micrometres. Therefore, local surface modification and nanofabrication have been possible via pulsed arcs in air atmosphere. Third, particles with different compositions (metallic and ceramic), structures (uniform and core–shell) and sizes (few nanometres to micrometres) have been synthesized by intermittent arc plasmas in liquid phase. Such a technique permits to overcome limitations imposed by gas phase operation and enriches the scope of material fabrication. Finally, anodic arc discharges of carbon using pulsed power at low frequencies (1–5 Hz) have proven suitable for nanomaterial production in very stable conditions. Such arc technique generates carbon nanostructures with effective rates comparable to standard steady arc. A concept of circuit model that mimics anodic arcs constituted a valid approach to estimate plasma parameters. Also, a non-reactive route of MoS_2 few-layer synthesis by pulsed arc using powder precursor has been tested.

Despite the successful implementation of pulsed arc sources for nanosynthesis, full impact of this method on nanoscience and nanotechnology has not been delivered yet. First, the dynamics of particle growth in periodically changing plasma conditions must be explored. An approach would consist of tracking nanoparticle generation using *in situ* diagnostics like LII to provide particle sizes as a function of time. Secondly, pulsed arc plasmas at atmospheric pressure are very promising in the field of plasma-materials applications. The relative simplicity of pulsed arc process makes this technique adequate for the preparation of further nanomaterials with special optical and electronic properties, like transition-metal dichalcogenide monolayers, and, by programming a sequential deposition routine, possibly new van der Waals heterostructures for quantum materials applications. A step

Table 1. State of the art in technology of nanomaterial synthesis by pulsed discharges: advantages and drawbacks of the different plasma sources. HiPIMS = high power impulse magnetron sputtering. PECVD = plasma-enhanced chemical vapour deposition.

Plasma source	Plasma type	Pulse parameters	Plasma highlights	Deposition highlights	Limitations	References
Pulsed-DC	• Glow discharge	50–350 kHz	• Low pressure	• Tuneable film properties	Nanomaterials need conditioned substrates	Michler *et al* (1998)
	• Non-thermal	5–50% duty	• Adaptable to PECVD and sputtering	• Nanocomposites		Cespedes *et al* (2007)
		200–1000 V				Vijayaraghavan *et al* (2016)
HiPIMS	• Glow discharge	0.01–5 kHz	• Low pressure	• Conformal and dense films	• Target overheating	Kouznetsov *et al* (1999)
	• Non-thermal	<1% duty	• Strong ionization	• Nanocomposites	• No nanomaterials	Sarakinos *et al* (2010)
		200–1000 V	• Adaptable to PECVD			Anders (2017)
						Brenning *et al* (2020)
Pulsed cathodic arc	• Arc discharge	1–10 Hz	• Low pressure	• Ultrahard and ultra-thin films	• Particulates: filtering required	Boxman *et al* (1995)
	• Non-thermal	<10% duty	• Full ionization	• Nanocomposites	• No nanomaterials	Robertson (2002)
		10–30 V				Anders (2014)
Pulsed anodic arc	• Arc discharge	1–500 Hz	• Atmospheric pressure	• High throughput	• Heat-resistant substrate	Sugai *et al* (2003)
	• Local thermal equilibrium	1–20% duty	• Gradients in density and temperature	• Crystal quality	• Arc instabilities	Parkansky *et al* (2004)
		30–50 V		• Stand-alone nanostructures		Omurzak *et al* (2007)
						Corbella *et al* (2019c)

Table 2. Main contributions to nanomaterial synthesis by pulsed-DC arcs held at atmospheric pressure.

Motivation	Approach	Contributions	Challenges	References
Nanomaterial tailoring	High-temperature pulsed arcs	• Control of growth mechanisms and nanomaterial properties • Single- and double-walled CNT	Lower gas temperatures	Sugai *et al* (1999a), Sugai *et al* (2003), Muhl *et al* (2005), Roch *et al* (2007)
Localized growth	Micro electro-discharge system	• CNT grown on ≈100 nm^2 areas with 0.01 mm separation	Higher spatial resolution	Parkansky *et al* (2004), Tsai *et al* (2009)
Environmental flexibility	Plasma in liquid phase	• Multicomponent nanoparticles • Core-shell structures (metal@C), fullerenes, and MWCNT	More stable liquid medium	Imasaka *et al* (2006), Omurzak *et al* (2007), Abdullaeva *et al* (2012), Kim *et al* (2021)
Efficiency and stability	Pulse configuration and diagnostics	• Modelling of anodic arc discharge • Deposition of MoS_2 layers	Higher material purity	Murooka *et al* (2001), Corbella *et al* (2019b), Corbella *et al* (2020a)

further could consist of optimizing growth process of nanomaterials by taking advantage of the natural self-organization faculty of plasmas, described as a spontaneous transition from a homogeneous stable state to a regular pattern in a spatially extended system. The coherent structures generated by plasma self-organization tend to modulate plasma chemistry and composition, including reactive species, electric field, and charged particles. Hence, by adopting *in situ* monitoring techniques, arc technological parameters, like discharge power and pulse frequency, could be conveniently adjusted to render nanosynthesis more efficient.

Acknowledgments

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Fusion Energy Sciences program (Award No. DESC0015767) and by the National Science Foundation (NSF) (Grant No. 1747760).

Data availability statement

No new data were created or analysed in this study.

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