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Progress in in-situ synthesis of graphitic carbon nanoparticles with physical vapor deposition

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Abstract

Graphitic carbon nanoparticles are in high demand for sensing, health care, and manufacturing industries. Physical vapor deposition (PVD) methods are advantageous for in-situ synthesis of graphitic carbon particles due to their ability to produce large area distributions. However, the carbon particles can agglomerate, irrespective of the PVD method, and form coagulated structures while growing inside the vacuum chamber. The random shapes and sizes of these particles lead to non-uniform properties and characteristics, hence making them less attractive for numerous industrial applications, such as energy storage batteries and structural health monitoring. Therefore, the in-situ synthesis of isolated carbon particles produced in a single-step PVD process having control over size, shape, and large area distributions has remained inspiring for the past 30 years. This article gives an overview of characteristics, applications, industrial impact, and global revenue of graphite particles. A critical review on in-situ growth of graphitic carbon particles with different PVD methods is described with selected examples. A comprehensive summary compares the capability of different PVD techniques and corresponding carbon resources to produce graphitic particles with numerous sizes and shapes. Analysing the outputs of various PVD methods, a generalised four-stage model is explained to understand the in-situ growth of graphitic carbon particles, which start from seedings and grow as particles, clusters, and granular structures. It is concluded that the isolated carbon particles can be produced with specific size, shape, and distributions irrespective of the PVD method employed, by maintaining precise control over combinations of deposition system properties and process parameters.

Keywords: Nanomaterials; Carbon; Graphitic; In-situ synthesis; Particle growth; Isolated nanoparticles; PVD; Engineered Particles

1. Introduction

Graphitic carbon particles [1] are widely used for structural health monitoring [2], medical treatment [3], sensing technology [4], cutting tools [5], and tribological applications [6]. These graphitic particles are recognised to regulate electrical conductivity [7, 8], thermal management [9,10], damping capacity [11,12], corrosion resistance [13,14], and wear resistance [15-17] in numerous industrial products. Their usability in advanced engineering applications is rapidly increasing. For example, electric batteries [18-20] with constantly increasing industrial demands, use graphitic carbon particles to improve their electro-chemical properties. Similarly, graphitic particles have proven their performance for aluminium machining [21] due to low-friction and energy-efficient features. Their demand in the cutting tool industry [22] has accelerated due to a surge in aluminium-consumed electronic products such as laptops, mobile phones and similar gadgets. Therefore graphitic carbon particles are actively being researched due to their superior performance for multiple industrial applications. Referring to Fig. 1, it can be seen that the number of research outputs on carbon particles has increased by over 500 % in past 20 years, from 11,743 publications in 2000 to 72,075 in 2020. Similarly, Fig. 2 presents the current and projected global revenue of the graphite market which is progressively increasing due to its high demand. The overall graphite market had an estimated value of USD 12.5 billion [23] in 2016, USD 14.3 billion [24] in 2019 and is projected to grow to USD 18.2 billion [23] by 2021 and USD 21.6 billion [24] by 2027. For granular and powder forms in particular [24], a global market value of USD 70 million was recorded in 2018 and is now forecasted to reach USD 82 million by 2025 with a compound annual growth rate of 1.8 %.

Figure 1.

Figure 2.

Carbon nanoparticles synthesis originated from carbon coatings which were originally discovered in 1953 [26]. In the 1960s, carbon coatings contained graphite-like features and remained popular for biomedical [27] and nuclear [28] applications. In the 1970s, carbon

coatings exhibited attractive mechanical properties by achieving higher sp^3 fractions [29] when investigated with different deposition methods and conditions. Thus, a new class of carbon coatings emerged in the early 1980s, having diamond-like features. These coatings were recognised as diamond-like carbon (DLC) coatings having a distinguished hardness, low friction, and higher scratch resistance. Investigations into DLC coatings have since produced three research streams; (1) improvement in DLC quality and resolving limitations; (2) commercialisation and re-coating; and (3) exploring the fundamental mechanisms and building blocks which combine to produce such superior carbon films.

Referring to the third stream, i.e., investigating the fundamental building blocks of carbon coatings, the synthesis of C₆₀ in 1985 with laser irradiation of graphite [30], helical graphite microtubes [31] and carbon nanotubes produced in 1991 [32] with arc discharge evaporation were revolutionary milestones. The attempts for in-situ synthesis of carbon particles were also reported in parallel. The literature review reflects that high-energy sources, such as sputtering, electron beams, lasers, and arc discharges were common methods used to produce carbon particles, as summarised in Fig. 3A. The difference in fundamental principles and operational parameters of PVD methods also bring variance in growth, crystal structure, morphology etc. of engineered graphitic carbon particles. crystal structure may vary with interplanar distance, crystal (ordered) and amorphous (disordered) arrangement of carbon atoms, defects, and structural growth in solid or hollow form. The said growth features influence particle morphology, density, and surface area which modifies their properties such as electrical and thermal conductivity, elasticity, absorbance, reflection, and chemical inertness to tailor their performance for different engineering sectors, such as, energy and environment, sensing, biological and chemical reactions, and for mechanical applications as shown in Fig. 3B. Irrespective of the synthesis method, the carbon particles usually agglomerate [33] due to higher electronegativity [34] and collisions inside the plasma which may reduce their performance for engineering applications, such as sensing capabilities. It is observed that the in-situ synthesis of isolated carbon particles was intensively investigated between 1990 to ~2005. Afterwards, alternative methods of carbon particle and nanostructure fabrication have emerged due to persistent agglomeration issues encountered during continued attempts made with physical vapor deposition (PVD). However, the in-situ synthesis of isolated carbon nanoparticles with PVD, having a specific size and large area distributions still remains inspiring [35-37].

Figure 3.

This article briefly describes the characteristics of graphite particles, such as the significance of crystal structure on corresponding properties, followed by an overview of their industrial applications in energy and environment, bio-chemical and medical, sensing technology, and structural and tribology sectors. The article presents refined examples of graphitic carbon particles produced with different PVD methods. A series of developments from agglomerated to isolated graphitic carbon particles have been summarised. A qualitative comparison is tabulated to reflect the in-situ growth of graphitic particles made with different PVD methods. A four-stage model for in-situ growth of isolated graphitic particles is explained to highlight the role of system and process influencers, irrespective of the synthesis method employed.

2. Characteristics of graphite carbon particles

Graphitic carbon particles have theoretical properties [38] similar to graphite but in practice they vary with synthesis method, which governs the growth mechanism and brings variations in their **crystal** structure, such as, crystallite height, interlayer distance, number of defects, or variation by structure and morphology, like sizes, shapes, porosity etc. These disorders in crystal structure are normally studied with X-ray powder diffraction (XRD) and Raman spectroscopy to evaluate the characteristics of graphite particles. Figure 4 presents the XRD $\theta - 2\theta$ scans (Fig. 4A) and Raman **spectrum** (Fig. 4C) of a hollow graphitic particle (Fig. 4B). Graphitic particles generally show an intense peak (002) around 25° [39] to 28° 2θ angle. Peak sharpness or slight variation in peak position reflects the crystallographic features, such as interlayer distance. Normally, the interlayer distance is found at ~ 0.34 nm for polyhedral graphite particles [40], onion-like particles [41], and hollow graphitic particles [42]. Besides in-situ synthesis, the crystallographic parameters are also sensitive to ex-situ procedures, such as chemical treatments which produce defects [41] in graphite particles and consequently change crystal dimensions. Similarly, the interlayer distance may differ between natural (0.3354 nm Nippon, Japan) and synthetic (0.3356 nm Hitachi, Japan) graphitic particles [43]. In the same way, the crystallographic structure may change with service life as graphitic particles used for lithium-ion batteries have shown variance in interlayer distance between 0.3365 nm to 0.4170 nm against different charge-discharge cycles [41]. Similar characteristics are measured with Raman spectroscopy, where the ordered and disordered carbon atoms show their peaks at specific wavelengths. **Raman spectroscopy is carried out with different laser**

wavelengths which could be from the ultraviolet to infrared spectral range depending on the material under investigation. Diamond and graphite show sharp peaks at 1332 cm^{-1} and 1580 cm^{-1} [44] when excited with a 514 nm wavelength laser. Thus, the corresponding peaks of disordered (D-band) and ordered (G-band) carbon atoms appear across said reference values and the variations in their positions specify their structural configurations. Onion-like particles, hollow graphitic particles, and polyhydric graphite particles have shown D-band structure at around 1340 cm^{-1} [41], 1349 cm^{-1} [42] and 1360 cm^{-1} [40], respectively. Whereas the corresponding G-band for onion-like particles and polyhydric graphite particles were found at 1580 cm^{-1} and 1573 cm^{-1} for hollow graphitic particles, respectively. Irrespective to the crystal structures obtained from in-situ synthesis [45], ex-situ conditions like pressure [46], temperature and oxidation also change the crystal structure and corresponding peak positions. The G-band shifts from 1580 cm^{-1} to 1600 cm^{-1} once the crystal structure transforms from graphite to a nano-graphite [47] structure. More details on crystal structure measurements of graphite particles can be found in the literature [48].

Figure 4.

Change in crystal structure significantly changes the corresponding properties of graphitic particles, such as density and surface area which in turn alters their electrical, mechanical, chemical, and thermal behaviours. It is observed that the increase in interlayer distance of 0.3354 nm of natural graphite particles to 0.3356 nm for synthetic graphite has increased the first-cycle efficiency of lithium-ion batteries from 82 % to 88 % [43]. Furthermore, a reverse trend has been observed [49] between density and resistivity, which suggests that the electrical resistivity increases from 0.009 to 0.022 Ωm with a decline in density from 2030 to 1860 Kg/m^3 . Similarly, referring to the effect of particle size and surface area, it can be estimated that graphitic particles of 4 μm , 14 μm , and 44 μm size, correspond to specific surface areas of 26 m^2/g , 12 m^2/g and 9 m^2/g respectively [50]. Similarly, the graphitic particles of 70 μm , 430 μm , and 960 μm size, present expandable ratios of 40, 380 and 400, and potential of hydrogen (PH) values of 3.25, 3.85 and 5.62 respectively [51]. The higher expandability of graphitic particles is associated with their larger particle sizes as thermographic analysis also reflects large expandability of 300 ml/g for 196 μm large size particles, whereas small size particles of 39.8 μm correspond to small expandability of only 40 ml/g [52]. Hence, the crystal structure i.e. interplanar distance, atomic arrangement, defects and physical aspects such as size, shape, surface area, and density, significantly influence the

electrical, thermal, and structural properties of graphitic particles. These properties are the bases of their functionality in different engineering applications in energy and environment, sensing, bio-chemical and medical and structural integrity sectors as summarised in Table 1.

Table 1. Applications of graphite particles in energy, environment, sensing, bio-chemical, medical, and structural domains. More details on synthesis and industrial applications of graphitic particles can be studied from the literature [53-106].

Energy and Environment	Sensing Technology	Bio-chemical and Medical Technology	Structural Integrity
Energy storage batteries [58-60]	Electro-chemical sensors (e.g., heavy elements detection) [65]	Water treatment [73,74]	Tribology [88-91, 104]
Fuel Cells [42]	Thermo-resistive sensors (flow and temperature sensor) [66]	Enzymatic catalysis [76]	Structural properties [84-87, 105, 106]
Fuel additives [64,89]	Biomedical sensors [69]	Drug delivery and gene therapy [77-79, 103]	Fire-retardant and corrosion resistance [92-97]
Solar energy [55-57]	Structural Health Monitoring [70,71]	Bioimaging [78,81,82]	3D manufacturing with conductive inks [100, 102]

3. In-situ synthesis of carbon nanoparticles with PVD

In-situ synthesis of graphitic nanoparticles has been reported with different methods, such as catalytic processes [107, 108], chemical vapour deposition [109], or physical vapor deposition (PVD) methods like irradiation [110], vaporisation [111], sputtering [35], and arc discharge [40] techniques. This review article covers PVD methods used for in-situ synthesis of agglomerated-to-isolated graphite particles with selected examples.

3.1 In-situ synthesis of graphitic particles with irradiation and vaporisation methods

Carbon nanoparticles were originally produced by irradiating carbon enriched resources, like diamond or graphite, with electron beams and laser beams. In 1992, Ugarte [110] reported the curling and closure of graphitic networks produced with electron beam irradiation and observed them with a transmission electron microscope (TEM) as shown in Fig. 5A. The irradiation produced a cluster of spherical graphitic nanoparticles having random diameters. It was demonstrated that 10 min of irradiation produces a mixture of tubular or polyhedral particles which transform into needles and spherical-like particles. Perfect sphericity develops after 20 min of irradiation and no further change in shape is observed for longer irradiations. Similarly, Fig. 5B presents TEM micrographs of graphitic particles made

with CO₂ laser vaporisation in conjunction with argon gas having a pressure of 0.8 MPa. It can be seen that the particles have polyhedral shapes which also vary size. It was deduced that the radiation and vaporisation methods have poor control over particle growth. The graphitic carbon particles of random size and shape agglomerate with each other to form clusters. Further details on particle synthesis with irradiation and vaporisation methodologies can be found in the literature [112-114].

Figure 5.

3.2 In-situ synthesis of graphitic particles with arc systems

The arc method intrinsically discharges micro carbon particles [115] from a cathode. These micro carbon particles were presumed as defects in thin carbon films and likely to reduce the coating properties [116]. Thus, single bend, double bend, and T-shaped cathodic arc systems were developed to filter out the contamination i.e., the micro-particles, while transporting the plasma from target-to-substrate. In contrast, the engineering of carbon nanoparticles of specified features was also attempted with cathodic arc systems. Amaratunga [117], Chhowalla [118, 119], and Roy [120], have documented their attempts to produce carbon particles with cathodic vacuum arc systems in 1996 and afterwards. The graphite target was arced in a high-pressure nozzle and the plasma was quenched with helium gas. However, the received nanomaterials contained a mixture of carbon nanotubes, hollow carbon nanoparticles, or carbon onions that were transported from source-to-substrate under a large pressure gradient. Besides a physical mixture as shown in Fig 6A, these nanomaterials exhibit a complex chemical composition including C₂, C₂₀, C₃₀, C₆₀, and C₇₀. The carbon coatings made of said mixtures have demonstrated superior mechanical performance i.e., higher hardness of 56 GPa and remarkable elasticity up to 85%. Similarly, Fig. 6B presents the synthesis of carbon onions of various sizes produced by cathodic vacuum arc. It is postulated that the carbon atoms, originating from the arc source, already possess higher kinetic energy, while the additional kinetic energy added by the quenching gas increases the momentum and reduces the mean-free-path. This stimulates their agglomeration while transporting them through a higher-pressure gradient, resulting in a physical mixture of nanomaterials arriving at the substrate surface. Similarly, Fig. 6C and Fig. 6D present the nanohorn and polyhedral graphitic particles produced with arc discharge using different precursors and experimental conditions. It is deduced that the arc method also produces clusters, agglomerations, strings, nanohorns, onions,

and their hybrids. More details on graphitic particles synthesis with arc discharge can be found in the literature [39, 40,121,122].

Figure 6.

3.3 In-situ synthesis of graphitic particles with sputtering

The in-situ synthesis of graphitic carbon particles with sputtering was also started in the early 1990s. Praburam and Goree [123,125] have reported sputtering based investigations to produce graphitic carbon particles. The self-biased graphite electrodes were exposed to radio-frequency glow to grow carbon nanoparticles from dusty plasma. The exposure time governs the physical appearance of nanomaterials, such as the formation of grains at 20 min and coagulated strings after 7 hours of exposure. Fig. 7A presents scanning electron microscopy (SEM) images of isolated coneflower-like carbon grains produced with an agglomeration of carbon dust, fullerene, or tinny nanoparticles with increasing exposure time. Similarly, for a longer exposure, such as 7 hours, the coagulated strings were formed by interconnecting of carbon particles having different sizes as shown in Fig. 7B. The group have also demonstrated the in-situ synthesis of raspberry-like carbon grains [125]. It is important to note that a cloud of fine carbon dust may be excreted at the start of the sputtering process due to absorbed water vapours and degassing [126]. Such fine dust may act as seeds for graphitic particle growth or could be considered as contamination for thin film depositions. In summary, time governed transformation from grains to coagulation/agglomeration has been observed through dusty plasma synthesis. Referring to Fig. 7C and Fig. 7D, the formation of carbon mixture (small and large particles, coneflower grains, linked networks, radial columns) and flakes were observed when produced with gas-phase sputtering in a tokamak plasma [127]. Usually, the in-situ synthesis of carbon particles was attempted in large vacuum chambers. However, a major step toward the in-situ synthesis of isolated carbon particles was observed in 2012 when Bouchat et al, [35] produced isolated and agglomerated particles by sputtering inside an aggregation tube installed within the sputtering chamber. The preliminary investigations yielded agglomeration (Fig 7E) or linked carbon particles (Fig. 7F). However, precise control over process settings i.e., pressure gradient and electric potential have produced uniformly distributed and isolated carbon nanoparticles having similar sizes and shapes, as shown in Fig. 7G. A controlled pressure gradient was maintained inside the aggregation tube, and particle isolation was enhanced with electrostatic potential. For commercial-scale manufacturing, the aggregation tube is considered as a limitation to produce graphitic carbon

particles with large area distributions. More details on carbon particles synthesis with sputtering can be studied from the literature [128-133].

Figure 7.

The work by Bouchat et al. [35] has demonstrated that isolated carbon particles can be created in common (large) chambers if precise control over the system and process is maintained. A small aggregation tube can be presumed as a sputtering chamber as long as a unique combination of electrostatic potentials, pressure gradient, substrate biasing, target-to-substrate distance and plasma kinetics can be controlled, which is practically challenging. Recently, isolated graphitic carbon particles [134] have been created in-situ with an unbalanced magnetron sputtering (UDP 650 Teer Coatings, UK, large chamber of 650 mm diameter \times 650 mm height) through rapid plasma quenching. The argon plasma was quenched with helium pulses to produce the particles of certain size i.e., ~ 50 , ~ 110 , ~ 350 , ~ 500 and ~ 800 nm; and isolation distances of less than $5 \mu\text{m}$, between 5 to $10 \mu\text{m}$ or more. An intensive parametric study with 48 parametric combinations was performed to identify the optimum conditions which provide control over the system and process to create spherical, uniform size, and large area distributed graphitic carbon particles. The most influential process parameters were helium pulse-to-plasma orientation, target-to-substrate distance, helium flow rate, injection duration and pulse frequency. Fig. 8A and Fig. 8B show the high-resolution representative images of isolated carbon particles observed by field emission scanning electron microscopy (FE-SEM), whereas their large area distributions are shown in Fig. 8C. The isolated carbon particles have shown superior mechanical and tribological performance when simultaneously embedded [135] in an amorphous carbon matrix in a single step process [87,136]. Further investigations [137] considering the effect of helium pressure and ultrashort pulses have demonstrated that a particle size 50 ± 10 nm with an isolation distance of less than $1 \mu\text{m}$ can further improve the material's performance.

Figure 8.

3.4 Summary of in-situ synthesis of graphitic particles with PVD methods

Table 2 describes the most refined examples of in-situ synthesis of graphitic carbon particles produced with different PVD methods, such as electron beam irradiation, laser irradiation, laser vaporisation, arc discharge, direct current (DC) and radiofrequency (RF)

discharges and magnetron sputtering. Each example is detailed with carbon source, particle size range, nature of outcomes i.e., isolated, conjugated, mixture by size and shapes. Similarly, essential process parameters specific to the method and corresponding outcomes are also remarked. More details and specifications on each PVD method can be studied from the related reference.

Table 2. PVD methods for in-situ graphitic carbon particles synthesis – refined examples.

Synthesis Method	Year	Carbon Source	Particle size (nm)	Conjugated /Coagulate	Mixture*	Isolated particles	Remarks	Ref
Electron Beam Irradiation	1992	Carbon soot	47-70	√	√	×	20 min irradiation brings specificity in particles	110
	1996	Diamond crystals	3-8	√	√	×	Intense electron beams of electron flux density of about 10^7 electrons/nm:	112
Laser Vaporisation	2004	Graphite target	40–60 80–100 190–350	√	×	×	Nanohorns, Polyhedral, High temperature, High pressure	46
	2007	Carbon dioxide	500-1000	√	√	×	Ultraviolet irradiate of near-critical carbon dioxide	113
	2009	Carbon powder suspension	1-6	×	√	√	Fluorescent carbon nanoparticles	114
Arc Discharge	1995	Graphite, Isopropanol, Nickel/Iron	5-10	√	√	×	String, Multi-shell	37
	1996	Graphite target	-	√	√	×	Mixture of closed, hollow graphitic carbon particles, CNT, and Carbon Onion. He quenching	117
	1997	Graphite rods	5-20	√	√	×	Mixture of Fullerene (Onion and bucky balls), CNT, and a-C	119
	2003	Water submerged graphite electrodes	5-50	√	√	×	Carbon onions	120
	2004	Carbon rod	~50	√	×	×	Nanohorns, high temperature	121
	2015	Hexan, Ethanol, Graphite electrodes	40-50	√	√	×	Onion-like carbon nanoparticles	39
	2018	Carbon rod, Ethanol	220-380	√	√	×	Polyhedral	40
RF Discharge / Sputtering	1994	Graphite rods	10-250	√	√	×	String, cauliflower-like surface	124
	1996	Graphite targets	~150, ~300 400-500	√	√	×	Grains, string	123

	1999	Graphite cathode	343±11	√	√	×	Bumpy spherical shape	129
	2006	Graphite cathode	50-200,000	√	√	×	Mixture of dust, small, and large particles, linked network, grains, flakes, and cauliflower structures	127
DC Discharge / Sputtering	2007	Graphite cathode	54±10	√	√	×	Cauliflowerlike grains	130
	2013	Polycrystalline graphite	~30 ~45	√	√	×	Particle size as a function of time	133
DC Magnetron Sputtering in aggregation tube	2011	Graphite cathode	12±2 10-20	√	×	√	Sputtering in aggregation tube, isolated particles, nanoribbons, pulverisation gas	35
	2017	Graphite cathode	50±10, 110±20	×	×	√	He quenching, Controlled size and isolation, Large area distribution.	134
RF Unbalanced Magnetron Sputtering	- 2019	Graphite cathode	~350 ~800	×	×	√		- 137

*Mixture by size and shape or mixture of isolated and conjugated particles

Fig. 9 shows the range of particles size produced with different PVD methods as analysed in Table 2. It can be seen that magnetron sputtering and laser vaporisation have the ability to produce isolated carbon particles at specific experimental conditions.

Figure 9.

4. Four-stage model for qualitative control over graphitic carbon particles growth

The literature review reflects that graphitic carbon particles coagulate [15] and agglomerate irrespective of the selected synthesis method; either arc discharge, laser irradiation, or sputtering. Fig. 10 presents a four-stage model [134] to understand the in-situ particle growth and synthesis of graphitic carbon particles with PVD methods. Usually, the carbon atoms leave the target and pass through the so-called stable plasma and deposit a homogeneous carbon film at the substrate surface. However, most in-situ synthesis mechanisms used to produce carbon particles with PVD methods, require plasma turbulence to achieve the objectives. For example, plasma quenching [117, 135] which is practised for in-situ synthesis of carbon particles, abruptly changes the plasma equilibrium and alters the plasma physics and chemistry. The quenching gas increases the chamber pressure and adds additional kinetic energy to the plasma system which influences the charge distributions, particle trajectories, mean-free-paths, and atomic/particles/molecular momentums. The mean-free-path is reported to reduce from ~

2.6×10^{-2} m to $\sim 0.2 \times 10^{-2}$ m with an increase in chamber pressure from 20×10^{-2} to 2×10^{-2} Torr [138]. The appropriate selection of quenching gas is also a sensitive parameter which regulates plasma dynamics. Comparing helium with argon, both gasses will have different mechanistic behaviours due to difference in their ionisation potential, molecular weights, and number of molecules per unit volume which govern the collisions, kinetics, and momentums. The injection: duration, frequency, flow rate, and pressure further exaggerate the plasma dynamics. Thus, particles growth is a complex mechanism and involves numerous factors, such as ion energies associated with kinetics, ion flux, ion and neutral drags, thermophoretic, electrostatic, and magnetic [139] potentials, electronegativity, gravity effects, pressure gradients, physical collisions and reversible transformation between stable carbon atoms and carbon ions.

As demonstrated by Praburam and Goree [125], particle growth is a time-dependent parameter [129]. Referring to Fig. 10, carbon leaves the cathode at the atomic scale, termed as seeds which grow in size and reach the phase of coalescence by absorbing carbon ions and stable carbon atoms [123] due to natural and forced (due to quenching gas) collisions. The material properties like elasticity and physical features like surface roughness also contribute towards the merging of particles. Similarly, the velocity of the collision must be lower than the threshold speed, which shall facilitate stacking of particles through van der Waals attractions. Otherwise, the particles will bounce apart in the case of higher collision speeds [140]. Along with physical collisions, a covalent bonding develops between host and incoming atoms/ions due to electronegativity difference [141]. The same mechanism repeats to transform particles into agglomeration and clustering phases. Finally, the clusters further combined to form macrostructures or a granular film at the substrate surface. Referring to time-dependent particle growth [125,127], the particles grow in isolation in the first 20 min of plasm glow exposure and then start inter-connecting with each other to form coagulations at around 2 hours. It is also worth mentioning that that coagulation is not an infinite process. The particle or cluster size and shape depends on the material's electronegativity, ion flux [123] and charge distribution over the surfaces and is administrated by the electrostatic potential of adjoining particles/clusters [142]. Similarly, electronegativity has an evident role in particle shape since it is anticipated to encounter surrounding potential. Generally, carbon with higher electronegativity (2.55) tends to maintain sphericity when compared with silver (1.93) which exhibits compact aggregate but close to a spherical shape, or copper (1.90) and aluminium (1.61) which form fractal-like particles due to lower electronegativity. The higher electrostatic potential is likely to increase the particles isolation [35], while in contrast, the increase in chamber pressure and addition of kinetic energy from an external source, like quenching gas,

reduces the mean-free path and accelerates the transformation from seeding to clustering. Therefore, the identification of optimised combinations of process parameters is essential to produce isolated carbon particles specific to that PVD system.

Figure 10.

The in-situ synthesis of isolated carbon particles has remained inspiring [17,18, 37] for the past thirty years. The recent investigations of isolated carbon particles synthesis with helium pulses [87,134-137] demonstrates that the in-situ synthesis of large area, uniformly distributed, isolated carbon particles produced in a single step process without supplementary instrumentation (like aggregation tube) is possible with precise control over system settings i.e., bias voltage, target-to-substrate distances, quenching methodology, and parameters, such as pulse orientations, flow rate, pressure, time etc.

Empirically, the particle size can be controlled by estimating the growth rate through Eq. 1 [123],

$$\frac{d_a}{d_t} = \frac{YJ_iT^3}{e} \quad (1)$$

Where a is particle radius, t is time, Y is sputtering yield, J_i is current density supplied to an electrode, T is the layer thickness formed by absorbed atoms, and e denotes electrons. Other empirical models describing collisions, atomic flux, energy distributions, energy interaction between particles and coagulation rate can be studied in the literature [127, 143,144]. However, the experimental investigations suggest that the in-situ synthesis of carbon particles is sensitive to system properties and operational parameters. The chamber size, target-to-substrate distance, pressure gradient, target currents and bias voltages, electrostatic and electromagnetic potentials in the plasma regime, characteristic of quenching gas and quenching parameters greatly influence the particles growth. The core influencers in graphitic particles growth with PVD methods are listed in Table 3 and precise control of their combinations can produce isolated carbon particles of the desired size, irrespective of the PVD method.

Table 3. Core system and operational parameters which influence the in-situ synthesis of graphitic carbon particles through PVD methods.

<u>System and operational influencers (not limited to)</u>		
PVD system	Plasma dynamics	Quenching Mechanism
Chamber size, design	Electrostatic potentials/bias voltage	Quenching layout

Target-to-substrate distance	Magnetic field	Characteristics of quenching gas
Chamber pressure	Temperature	Operational parameters:
Electrode Current	Any other source which adds energy to the plasma	- Quenching time
		- Gas pressure
		- Flowrate
		- Injection frequency

Summarising the discussion, it is perceived that:

- A unique combination of process parameters may produce isolated carbon particles for any PVD system.
- There are higher chances to receive isolated particles in shorter process times.
- Electrostatic potential/bias voltage help in increasing isolation between particles.
- The isolation is likely to reduce with increasing pressure gradient inside the chamber.
- The isolation is likely to reduce by reducing target-to-substrate distance.
- Appropriate quenching gas and corresponding operational parameters should be optimised to identify those conditions which facilitate the growth of isolated graphitic carbon particles.

Conclusion

In-situ synthesis of isolated graphitic carbon particles with PVD methods is desirable for superior performance in numerous industrial applications. The role of crystal structure on the properties of graphitic particles and their applications in energy, environment, sensing, medical, and mechanical sectors are overviewed. Generally, graphitic particles agglomerate due to collisions and higher electronegativity. Hence, 30 years of progress with in-situ synthesis of carbon particles using PVD methods has been critically reviewed and those materials and procedures within the PVD domain which can produce isolated graphitic carbon particles have been identified. Four stages of particle growth are explained with system and operational influencers, to understand the graphite particle growth mechanisms. It is perceived that isolated graphitic particles can be created with specific size, shape, and distributions with any PVD system as long as a unique combination of system and process parameters are controlled precisely.

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Competing interest

The authors declare no competing interests.

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LIST OF FIGURES

Figure 1. Number of research outputs on carbon particles indexed at sciencedirect.com in past 20 years. Scientific outputs increased by over 500 % in past twenty years.

Figure 2. Global revenue of the graphite market. (A) Graphite including all types, and (B) Granular and Powder graphite only. Data adapted from public internet platforms [23-25]. The compound annual growth rate of granular and powder graphite comprises at least 25 % of the total graphite market.

Figure 3. (A) Physical vapor deposition methods commonly used for in-situ synthesis of graphitic carbon particles and (B) Application of graphitic carbon particles in different engineering sectors.

Figure 4. Representative (A) XRD $\theta - 2\theta$ scans and (B) Raman spectrum of hollow graphitic particle (C). Variance in peak intensities, widths, and positions is related to the crystal structure which determines the graphite properties and performance for industrial applications. Reproduced with permissions [42].

Figure 5. TEM images of graphitic carbon particles produced with (A) Electron beam irradiation of carbon soot (B) Laser vaporisation of graphite. Reproduced with permissions A [110] and B [111].

Figure 6. TEM images of (A) Mixture of carbon nanotubes and carbon particles, (B) Carbon onions, (C) Single-wall carbon nanohorn particles, and (D) Polyhydreal graphitic particles in-situ produced with arc technology. Reproduced with permissions A [119], B [120], C [121] and D [40].

Figure 7. SEM images of (A) Coneflower-like carbon grains and (B) Coagulated string of connecting graphitic carbon particles produced from graphite electrode-to-RF glow exposure; (C) Mixed structures and (D) Flakes produced from gas-phase sputtering; and (E) Agglomerations, (F) Linked chains, and (G) TEM image of isolated carbon particles produced inside an aggregation tube within the sputtering chamber. Reproduced with permissions A [123], B [124], C and D [127], E to G [35].

Figure 8. Representative FE-SEM images of (A, B) individual and (C) large-area uniform distribution of isolated carbon particles produced in an industrial-grade unbalanced magnetron sputtering system with rapid plasma quenching. Reproduced with permissions [134]

Figure 9. The capability of PVD methods to produce a range of graphitic carbon particles by size. In confined analysis, it is observed that magnetron sputtering and laser vaporisation can produce isolated graphitic carbon particles.

Figure 10. A generalised four-stage model to reflect the in-situ particle growth mechanism in PVD methods. Particles grow from seeding to coalescence and become atomic clusters before collecting to form a granular structure on the substrate surface. It is deduced that isolated graphitic carbon particles can be produced irrespective to PVD method and scale, if a precise control over system and operational parameters is maintained.

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