### PAPER • OPEN ACCESS

# Growth of metal nanoparticles in hydrocarbon atmosphere of arc discharge

To cite this article: S Musikhin et al 2024 Nanotechnology 35 385601

View the article online for updates and enhancements.

# You may also like

- <u>Copper induced hollow carbon</u> <u>nanospheres by arc discharge method:</u> <u>controlled synthesis and formation</u> <u>mechanism</u> Rui Hu, Mihai Alexandru Ciolan, Xiangke
- Rui Hu, Mihai Alexandru Ciolan, Xiangke Wang et al.
- Pulsed anodic arc discharge for the synthesis of carbon nanomaterials
  Carles Corbella, Sabine Portal, Denis B
  Zolotukhin et al.
- <u>Few-layer flakes of Molybdenum</u> <u>Disulphide produced by anodic arc</u> <u>discharge in pulsed mode</u> Carles Corbella, Sabine Portal, M A S R Saadi et al.

# Growth of metal nanoparticles in hydrocarbon atmosphere of arc discharge

# S Musikhin\*, V Nemchinsky and Y Raitses

Princeton Plasma Physics Laboratory, Princeton, NJ 08543, United States of America

E-mail: smusikhin@pppl.gov

Received 3 May 2024, revised 11 June 2024 Accepted for publication 21 June 2024 Published 1 July 2024

## Abstract

A direct current (DC) arc discharge is a widely used method for large-scale production of metal nanoparticles, core-shell particles, and carbon nanotubes. Here, the growth of iron nanoparticles is explored in a modified DC arc discharge. Iron particles are produced by the evaporation of an anode, made from low-carbon steel. Methane admixture into argon gas serves as a carbon source. Electron microscopy and elemental analysis suggest that methane and/or products of its decomposition adhere to iron clusters forming a carbon shell, which inhibits iron particle growth until its full encapsulation, at which point the iron core growth is ceased. Experimental observations are explained using an aerosol growth model. The results demonstrate the path to manipulate metal particle size in a hydrocarbon arc environment.

Supplementary material for this article is available online

Keywords: core-shell nanoparticles, methane, arc discharge, sustainability, carbon nanotubes, metal nanoparticles

# 1. Introduction

Metal nanoparticles possess attractive magnetic, optical, and catalytic properties, which depend on the particle size [1-3]. This motivates developing tools to control the size distribution of metal particles during their synthesis. Creating a carbon shell over the metal core is one of these tools. For example, chemical vapor deposition (CVD) studies demonstrated that once the carbon shell is formed the metal core growth is ceased [4, 5].

Historically, however, the motivation for encapsulating metal nanoparticles was rather to protect the metal core from

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. oxidation and agglomeration and to provide chemical and thermal stability, so that particles retain their properties in different environments [6]. Applications of such core–shell particles vary from magnetic fluids [7], syngas conversion [8], hydrogen evolution reaction [9], and drug delivery [10], to carbon nanotubes (CNT) synthesis [11].

One of the dominant methods for single-step production of metal-carbon nanoparticles at a large scale is the direct current (DC) arc discharge [12–17], although other techniques have been used [18–23]. In the DC arc, the discharge is maintained between two electrodes, where an anode is usually made of graphite, which ablates and provides a feedstock of carbon for nanomaterials synthesis. Metal is typically added as a powder of microparticles, which evaporate in the hot arc and nucleate as nanoparticles.

Understanding and controlling metal particle growth is also relevant for arc discharge synthesis of CNT [24–29]. For example, catalyst particles larger than 5 nm are associated with the formation of multi-walled CNT (MWCNT),



<sup>\*</sup> Author to whom any correspondence should be addressed.

while single-walled CNT (SWCNT) typically require catalysts under 3–5 nm [30–33]. Although carbon coverage is commonly assumed to poison the catalyst, alternative experimental observations exist. Nagatsu *et al* [11], using a DC arc discharge, prepared Ni and Fe particles encapsulated in several graphene layers, which they later used as catalysts to grow MWCNT in a CVD reactor. Schunemann *et al* [5], observed growing tubes while they were surrounded by an amorphous carbon shell, and concluded that carbon feedstock can permeate through the shell and reach catalyst particles.

In this work, a modified arc approach was utilized where carbon feedstock is supplied by the decomposition of hydrocarbon gas (CH<sub>4</sub>) in the hot arc core, while the evaporating steel anode provides the metal (Fe). The use of a gaseous hydrocarbon instead of a consumable graphite electrode makes this method continuous and scalable for industrial production, which was successfully commercialized for carbon black [34] and CNTs [35]. Importantly, methane is the second most abundant anthropogenic greenhouse gas that is also 28 times as potent as  $CO_2$  at trapping heat in the atmosphere. By utilizing methane to produce high-value solid materials and hydrogen (not investigated here), we aim to make the process more sustainable. Given the scalability and sustainability of methane arc discharge to obtain high-value nanomaterials, it is important to develop an understanding of how metal aerosols grow in such environments.

The synthesis of metal-carbon core-shell particles using methane arc discharge was realized before [36-39]. Some studies also explored how the methane atmosphere affects particle size. Dong et al compared the sizes of particles synthesized by evaporating an iron anode at different CH<sub>4</sub> pressures [36]. The authors observed that the mean particle size decreased as methane pressure increased from 13.3 to 40 kPa. While the effect was clearly observed, its interpretation is not straightforward. First, there was no direct comparison of particles synthesized with and without methane, while keeping other conditions constant. Second, the authors compared the overall sizes of particles rather than the iron cores, leaving an option that changes were due to the carbon shell thickness. Finally, experiments were conducted at different pressures, which could have impacted plasma characteristics and aerosol growth kinetics [40, 41]. Hao et al compared the sizes of copper particles encapsulated with carbon that were synthesized using He/H<sub>2</sub> (1:1) and He/CH<sub>4</sub> (1:1) gas mixtures [37]. They found that in the presence of  $CH_4$ , carbon limited the copper particles aggregation and hence, reduced their size. However, when replacing a large part of the gas mixture with another gas (e.g. half of the mixture from H<sub>2</sub> to CH<sub>4</sub>), multiple arc parameters are expected to be affected due to different gas properties, such as specific heat capacity, and thermal and electrical conductivity [42]. Furthermore, the inconsistent particle sizes reported throughout the study complicate the interpretation of the results.

Here, we unambiguously demonstrate in an experiment and explain with an aerosol growth model that a carbon coating indeed inhibits the growth of iron nanoparticles formed from iron vapor in the Ar/CH<sub>4</sub> arc and that this effect alone is sufficient to obtain ultra-fine metal nanoparticles of only a couple of nanometers in size. Note that implementation of other size control knobs, such as adjusting the gas flowrates to vary species concentration and residence time or quenching to terminate the reaction kinetics, is limited in arcs, because of instabilities [43, 44] and strong gradients of species densities, temperature, and pressure [45].

# 2. Experimental setup and procedures

Experiments were carried out in a stainless-steel vacuum chamber (figure 1(a)). Electrodes, shown in figure 1(b), were oriented vertically inside the chamber, with a 6.4 mm diameter cathode on top (2% ceriated tungsten) and a 9.5 mm diameter anode underneath (A36 steel, Fe > 99 wt.%, C 0.06 wt.%). The anode was placed on a positioning stage so that the interelectrode gap was adjusted by a stepper motor. The gap was kept constant at 2–3 mm: electrodes separated enough, so that the melting anode does not weld to the cathode, but not too far from each other to stabilize the discharge. Furthermore, the constant interelectrode gap among multiple experiments suggests similar temperature fields and electrode ablation rates [45], and thus, allows for particle size comparison. The gap was continuously monitored with a camera and adjusted if necessary.

The reactor chamber was first pumped down to  $\sim 1$  Pa  $(\sim 10 \text{ m Torr})$  and subsequently filled with a working gas mixture to a pressure of 67 kPa (500 Torr). Two cases were investigated: Ar (5.0 purity) flow of 916  $\pm$  5 sccm; and a mixture of Ar (916  $\pm$  5 sccm) and CH<sub>4</sub> (22.9  $\pm$  0.1 sccm, 4.0 purity) flows, which corresponds to a 2.4 wt.% CH<sub>4</sub> in Ar. All gas flows were controlled by calibrated mass flow controllers (Alicat Scientific). The pressure inside the chamber was maintained at 67  $\pm$  4 kPa (500  $\pm$  30 Torr) and monitored with a pressure transducer (MKS, Baratron 221 A). The reactor was checked for leaks using a helium leak detector (Pfeiffer Vacuum), a typical leak was measured to be  $10^{-7} \cdot 10^{-8}$  Torr 1 s<sup>-1</sup>. The arc was ignited by a spark from a tungsten wire biased to 2 kV using a Bertan Associates Inc. (205 A-05 R) high-voltage power supply. The discharge was sustained with a Sorenson SGA100X100C-1AAA 100 V/100 A power supply, operated at a constant current of 33 A. The voltage measured across the two electrodes was 10-12 V in the case of pure Ar, and 12-16 V in the case of Ar/CH<sub>4</sub> mixture. The arc current was measured across a 2 m $\Omega$  shunt resistor, denoted in figure 1 as  $R_{\text{shunt}}$ . The current value was chosen based on the previous research in similar arcs (although with graphite electrodes), which showed that the low ablation regime at smaller currents (below 55 A for graphite) is more stable and allows for longer arc operation [46]. A typical run lasted for 1.5 h, limited by chamber heating. After turning the plasma off, the reactor was evacuated with the pump, filled with Ar to 80 kPa (600 Torr), and left for at least an hour to cool down.

Particle samples were collected for *ex situ* analysis in two ways, using (i) a PTFE-membrane particulate filter (Cobetter,



**Figure 1.** (a) Diagram of the experimental setup; (b) image of an arc in operation showing electrode diameters and the glowing spot size. The tungsten cathode (top in (b)) is fixed while the steel anode (bottom in (b)) position is adjusted with a stepper motor.

MFPT-2247) installed stationary in the exhaust vacuum line; (ii) a TEM grid (200 mesh Cu with a lacey carbon film) placed on the chamber bottom. In the former case, the filter collected particles carried with the gas flow to a vacuum pump. In the latter case, particles are deposited on the grid under gravity and free convection flow.

Particle morphology, size distribution, and chemical composition were analyzed using a scanning transmission electron microscope (STEM, FEI Talos FX200, 200 kV) with integrated energy dispersive spectroscopy (EDS, 20 kV). Powder collected on a particulate filter was scraped off, dispersed in absolute ethanol ( $\geq$ 99.5% purity), and ultrasonicated for 10 min to form a nanocolloid. One droplet of the nanocolloid was then deposited on a TEM grid for analysis. No difference was observed between such samples and the ones collected directly on a TEM grid placed inside the reactor.

#### 3. Experimental results

Figure 2 shows typical TEM images of nanoparticles synthesized in the arc reactor either in pure Ar (figures 2(a)– (d)) or in an Ar/CH<sub>4</sub> mixture (figures 2(e)–(h)). In both cases, fractal aggregates consisting of primary spherical particles were formed, which is typical for gas-phase syntheses [47]. In pure Ar atmosphere, primary particles are mainly composed of Fe and O, as shown in figure 3 top row by high-angle annular dark-field (HAADF) STEM and energy dispersive x-ray spectroscopy (EDS). Considering a small but non-zero leak in the chamber, the amorphous nature of the carbon shell, which is less efficient in preventing oxidation than a graphitized shell [48, 49], and that iron nanoparticles are prone to oxidation even at room temperature [50], particles could have oxidized inside of the reactor as well as outside, when extracted for analysis. Figures 2(e)–(h) shows dark aggregates enveloped in a light amorphous material. The chemical composition (figure 3 bottom row) suggests that the darker particles consist of iron while the shell is an amorphous carbon. EDS maps and TEM images show that, when adding methane to the system, iron particles get entirely coated with carbon. Based on the quantitative EDS analysis (background corrected, interactive TEM method), the carbon content in such samples was roughly estimated to be  $80 \pm 15$  wt.%.

Although not shown here for clarity, other trace elements were detected using EDS, namely Mn, Si, and Cu, coinciding spatially with iron nanoparticles, and each present at concentrations less than 5 at%. All three elements are known to be present in low-carbon A36 steel. However, since the applications of the obtained core–shell nanoparticles were beyond the scope of this study, the influence of these trace elements on particles performance was not investigated.

In some images (see supplementary information), discrete, non-aggregated iron particles were found, which were still embedded in amorphous carbon. No such discrete iron particles were observed in the case of pure Ar, only fractal aggregates. It suggests that carbon shells have formed early enough to prevent at least some iron clusters from coagulating and forming aggregates. That could have also limited iron particle growth by iron atoms adsorption and clusters coalescence. To check this, particle size distributions were experimentally measured for both working mixtures, with and without methane.

Iron particle size distributions are plotted in figure 4 as histograms of the probability density functions (PDF) along with lognormal fits, which yield count median diameters (CMD) and geometric standard deviations (GSD). More than 150 particles were measured to build each histogram. Multiple samples were analyzed but only two extreme cases, with the smallest and largest CMDs for each gas mixture, are shown



**Figure 2.** Typical TEM images of particles synthesized in pure Ar (a)–(d) or a mixture of 2.4 wt. % CH<sub>4</sub> in Ar (e)–(h). Methane addition led to iron-carbon core–shell particles formation.



**Figure 3.** HAADF STEM image and EDS elemental maps of aggregates synthesized in pure Ar (top row) or a mixture of 2.4 wt.% CH<sub>4</sub> in Ar. When adding methane, iron particles got covered by carbon.

in figure 4. Iron core size decreased from 8–11 nm in pure Ar to 3–5 nm when adding 2.4 wt.% CH<sub>4</sub> to Ar. This experimentally confirms that the carbon shell formation limits iron core growth. Furthermore, in the case of Ar/CH<sub>4</sub> mixture, the obtained catalyst particles were under 5 nm, which is expected to favor SWCNT formation relative to MWCNT and soot [30–32, 51]. However, the efficient synthesis of SWCNT was not the goal of this work, hence, we did not manipulate any other process parameters, e.g. pressure, gas temperature, precursor/catalyst types, and their concentrations [52, 53]. This explains why only a small number of SWCNT was detected in the Ar/CH<sub>4</sub> sample (figure 2(f)). The efforts to improve SWCNT yield in the methane arc discharge are currently ongoing.

#### 4. Discussion

To explain experimental observations, we refer to the aerosol growth model from [54], which uses a commonly accepted nucleation model by Girshick and Chiu [55], and accounts for condensation, evaporation, and coalescence. The model is extended to accommodate for the possibility of carbon atoms adhering to the metal cluster surface, which leads to carbon diffusion and shell formation. For the exact formulas and notations, a reader is referred to the original model publication [54], while here, for the sake of the 'proof of principle' analysis, simplified phenomenological terms are used. Schematics of the considered processes are depicted in figure 5.



0.35

0.30

0.25

0.20

0.15

0.10

0.05

PDF / nm<sup>-1</sup>

Ar/CH<sub>4</sub>

5

CMD = 3.3 nm

Ar/CH<sub>4</sub>

CMD = 4.8 nm

CMD = 8.1 nm

CMD = 11.3 nm GSD = 1.4

20

GSD = 1.4

15

GSD = 1.6

10

Figure 4. Iron particle size probability density functions (PDF) and corresponding lognormal fits. CMD: count median diameter, GSD:

geometric standard deviation. For Ar/CH4 mixtures, the methane

Diameter / nm

GSD = 1.5



The rate change of cluster density is given by

$$\frac{\partial N_{\text{cluster}}}{\partial t} = N_{\text{nucleation}} - N_{\text{coalescence}} (1 - \theta)^2.$$
(2)

Cluster density increases due to nucleation of new clusters and decreases due to coalescence. Parameter  $(1-\theta)^2$  describes a probability of two iron clusters coalescing, where each cluster has a  $1-\theta$  part of its surface not occupied by carbon.

First, let us briefly describe a process of iron aerosol growth by inert condensation. As iron atoms evaporate from the anode surface, they diffuse into and collide with argon buffer gas and cool down. At the same time, when moving away from the anode, the buffer gas temperature drops leading to iron atoms supersaturation, which prompts clusters nucleation [55]. Clusters grow by iron atoms adsorption and coalescence. Following our notation, both processes occur with  $\theta = 0$ in equations (1) and (2), due to the absence of hydrocarbons. Adsorption consumes iron atoms, decreasing the level of supersaturation. Furthermore, atoms and clusters diffuse into space, which reduces their densities as  $1/R^3$ , where R is the distance from the evaporation surface. At some distance, iron atom density drops to a level below supersaturation, so nucleation stops. The density of iron clusters also reduces with distance until virtually no coalescence occurs. Therefore, particle growth is limited by iron atoms and clusters expansion in space.

Next, we try to describe phenomenologically the process of iron aerosol growth in the hydrocarbon atmosphere. Simultaneously with iron cluster growth, CH<sub>4</sub> and products of its dissociation in the hot arc adhere to the cluster surface releasing carbon atoms. Carbon atoms then could diffuse inside the metal particle until its saturation and then precipitate on the surface (bulk diffusion) or directly accumulate on the surface forming 'islands', which grow in size (surface diffusion). The actual mechanism of the surface coverage with carbon is irrelevant to the purpose of this work. Importantly, once the metal cluster surface is fully covered with carbon atoms, i.e. when  $\theta = 1$ , its growth is terminated. As experimentally observed, at the chosen CH<sub>4</sub> partial pressure and arc parameters used in this work, the carbon shell formation becomes the limiting factor of iron particle growth rather than atoms and clusters expansion in space.

The described above growth saturation can be explained by analyzing equations (1) and (2). When looking into the second term of equation (1), a partially carbon-covered iron cluster,  $0 < 1 - \theta < 1$ , would have a limited surface exposed to metal condensation, decreasing the likelihood of iron atom adsorption, and slowing down cluster growth. When fully encapsulated in carbon, i.e.  $1-\theta = 0$ , adsorption stops, which

Figure 5. Schematics of iron particles growth near evaporating steel anode in a hydrocarbon atmosphere. Not up to scale. Considered processes: (i) evaporation of iron from a hot molten anode surface;

(ii) iron vapor diffusion into the cold argon gas, iron vapor cooling, and nucleation of clusters; (iii) clusters growth by iron atoms condensation and coalescence; (iv) thermal and thermocatalytic decomposition of hydrocarbons; (v) carbon adsorption, diffusion, and shell formation.

To follow the evolution of clusters size in time, we introduce the mean cluster volume defined as the ratio of the total clusters volume density,  $N_{\text{volume}}$ , to the cluster density,  $N_{\text{cluster}}$ . This monodisperse size approximation is often used in cluster growth models, e.g. in [54]. The rate change of  $N_{\text{volume}}$ , is given by

$$\frac{\partial N_{\text{volume}}}{\partial t} = V_{\text{nucleation}} + V_{\text{condensation}} \left(1 - \theta\right), \qquad (1)$$

where the first term on the RHS represents volume growth due to clusters nucleation, while the second due to condensation of is represented by the second term of equation (1) canceling out. A similar line of thought applies to equation (2), a partial coverage by carbon reduces the probability of clusters coalescing with each other, while a fully formed carbon shell,  $1-\theta = 0$ , cancels out the coalescence term in equation (2). Additional carbon atoms are still able to adhere to the shell increasing its thickness, but the iron core growth is ceased.

Apart from the straightforward applicability to core-shell particles, we argue that the process of slowing down the iron particle growth while the shell develops is also relevant to CNT synthesis. In situ TEM observations by Lin et al showed that the growth rate of a SWCNT on a Ni particle initially increased and then decreased until the growth terminated [56]. They attributed the decreasing growth rate to the continuous coverage of the catalyst with carbon, which passivated the active catalyst sites and gradually reduced its efficiency. In their molecular dynamics study, Ding et al proposed that more than one carbon island could form on a catalyst surface during the CNT nucleation [57]. Both studies suggest that coverage of the catalyst surface is a dynamic process occurring during tube formation and growth, which, as shown in our model, would inhibit catalyst size growth. We hope that this finding, explained here with a simplified model, will motivate the development of more comprehensive models capable of predicting the kinetics of metal particle growth in hydrocarbon arcs.

#### 5. Conclusions

We explored iron nanoparticles growth in the Ar/CH<sub>4</sub> arc discharge generated from evaporating steel anode. TEM and EDS analyses revealed that the core-shell iron-carbon particles that were formed in the Ar/CH<sub>4</sub> mixture had significantly reduced iron core sizes compared to particles grown in pure Ar. The simplified aerosol growth model was able to explain this result by incorporating a hydrocarbon environment and allowing carbon to adsorb onto the iron core. The process of carbon shell formation inhibited iron atoms adsorption and clusters coalescence, eventually leading to the full encapsulation and cessation of iron core growth. This shows the possibility of leveraging the intrinsic formation of the carbon shell on metal particles in hydrocarbon arc discharges, e.g., for the synthesis of core-shell structures and CNT with prescribed properties. A small number of SWCNT was also synthesized in this work, and the efforts to improve yield are currently ongoing.

#### Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

#### Acknowledgments

This work was supported by the U.S. Department of Energy through Contract DE-AC02-09CH11466. We thank Hengfei Gu and Bruce Koel (both Princeton University) for insights on material evaluation, the staff of Princeton University Image and Analysis Center for their help with TEM/EDS, and Timothy Bennett, Aleksandr Merzhevsky, and Nirbhav Chopra (all Princeton Plasma Physics Laboratory) for technical assistance and fruitful discussions.

#### **ORCID iDs**

- S Musikhin () https://orcid.org/0000-0002-0199-6095
- V Nemchinsky D https://orcid.org/0000-0002-6064-7354
- Y Raitses (b) https://orcid.org/0000-0002-9382-9963

#### References

- Kelly K L, Coronado E, Zhao L L and Schatz G C 2003 The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment *J. Phys. Chem.* B 107 668–77
- [2] Liu L and Corma A 2018 Metal catalysts for heterogeneous catalysis: from single atoms to nanoclusters and nanoparticles *Chem. Rev.* 118 4981–5079
- [3] Cuenya B R 2010 Synthesis and catalytic properties of metal nanoparticles: size, shape, support, composition, and oxidation state effects *Thin Solid Films* 518 3127–50
- [4] Xu Y, Ma Y, Liu Y, Feng S, He D, Haghi-Ashtiani P, Dichiara A, Zimmer L and Bai J 2018 Evolution of nanoparticles in the gas phase during the floating chemical vapor deposition synthesis of carbon nanotubes *J. Phys. Chem.* C 122 6437–46
- [5] Schünemann C, Schäffel F, Bachmatiuk A, Queitsch U, Sparing M, Rellinghaus B, Lafdi K, Schultz L, Büchner B and Rümmeli M H 2011 Catalyst poisoning by amorphous carbon during carbon nanotube growth: fact or fiction? ACS Nano 5 8928–34
- [6] Lu A, Salabas E L and Schüth F 2007 Magnetic nanoparticles: synthesis, protection, functionalization, and application Angew. Chem., Int. Ed. 46 1222–44
- [7] Odenbach S 2004 Recent progress in magnetic fluid research J. Phys.: Condens. Matter 16 R1135
- [8] Wang C, Zhai P, Zhang Z, Zhou Y, Ju J, Shi Z, Ma D, Han R P S and Huang F 2015 Synthesis of highly stable graphene-encapsulated iron nanoparticles for catalytic syngas conversion *Part. Part. Syst. Charact.* **32** 29–34
- [9] Jing S, Lu J, Yu G, Yin S, Luo L, Zhang Z, Ma Y, Chen W and Shen P K 2018 Carbon-encapsulated WOx hybrids as efficient catalysts for hydrogen evolution *Adv. Mater*. 30 1705979
- [10] Xu Y, Shan Y, Zhang Y, Yu B, Shen Y and Cong H 2019 Multifunctional Fe<sub>3</sub>O<sub>4</sub>@C-based nanoparticles coupling optical/MRI imaging and pH/photothermal controllable drug release as efficient anti-cancer drug delivery platforms *Nanotechnology* **30** 425102
- [11] Nagatsu M, Yoshida T, Mesko M, Ogino A, Matsuda T, Tanaka T, Tatsuoka H and Murakami K 2006 Narrow multi-walled carbon nanotubes produced by chemical vapor deposition using graphene layer encapsulated catalytic metal particles *Carbon* 44 3336–41
- Scott J H J and Majetich S A 1995 Morphology, structure, and growth of nanoparticles produced in a carbon arc *Phys. Rev.* B 52 12564–71
- [13] Si P-Z, Zhang Z-D, Geng D-Y, You C-Y, Zhao X-G and Zhang W-S 2003 Synthesis and characteristics of carbon-coated iron and nickel nanocapsules produced by arc discharge in ethanol vapor *Carbon* 41 247–51
- [14] Aguiló-Aguayo N, Inestrosa-Izurieta M J, García-Céspedes J and Bertran E 2010 Morphological and magnetic properties of superparamagnetic carbon-coated Fe nanoparticles

produced by arc discharge *J. Nanosci. Nanotechnol.* **10** 2646–9

- [15] Borysiuk J, Grabias A, Szczytko J, Bystrzejewski M, Twardowski A and Lange H 2008 Structure and magnetic properties of carbon encapsulated Fe nanoparticles obtained by arc plasma and combustion synthesis *Carbon* 46 1693–701
- [16] Corbella C, Portal S, Kundrapu M N and Keidar M 2022 Nanosynthesis by atmospheric arc discharges excited with pulsed-DC power: a review *Nanotechnology* 33 342001
- [17] Liang F, Tanaka M, Choi S and Watanabe T 2016 Investigation of the relationship between arc-anode attachment mode and anode temperature for nickel nanoparticle production by a DC arc discharge J. Phys. D: Appl. Phys. 49 125201
- [18] Eremin A V, Gurentsov E V and Musikhin S A 2016 Synthesis of binary iron–carbon nanoparticles by UV laser photolysis of Fe(CO) 5 with various hydrocarbons *Mater. Res. Express* 3 105041
- [19] Park J B, Jeong S H, Jeong M S, Kim J Y and Cho B K 2008 Synthesis of carbon-encapsulated magnetic nanoparticles by pulsed laser irradiation of solution *Carbon* 46 1369–77
- [20] El-Gendy A A, Ibrahim E M M, Khavrus V O, Krupskaya Y, Hampel S, Leonhardt A, Büchner B and Klingeler R 2009 The synthesis of carbon coated Fe, Co and Ni nanoparticles and an examination of their magnetic properties *Carbon* 47 2821–8
- [21] Luo N, Liu K, Liu Z, Li X, Chen S, Shen Y and Chen T 2012 Controllable synthesis of carbon coated iron-based composite nanoparticles *Nanotechnology* 23 475603
- [22] Zheng J, Liu Z Q, Zhao X S, Liu M, Liu X and Chu W 2012 One-step solvothermal synthesis of Fe<sub>3</sub>O<sub>4</sub>@C core-shell nanoparticles with tunable sizes *Nanotechnology* 23 165601
- [23] Liu B, Shao Y, Xiang X, Zhang F, Yan S and Li W 2017 Highly efficient one-step synthesis of carbon encapsulated nanocrystals by the oxidation of metal π-complexes *Nanotechnology* 28 325603
- [24] Shi Z, Lian Y, Liao F H, Zhou X, Gu Z, Zhang Y, Iijima S, Li H, Yue K T and Zhang S-L 2000 Large scale synthesis of single-wall carbon nanotubes by arc-discharge method *J. Phys. Chem. Solids* 61 1031–6
- [25] Journet C, Maser W K, Bernier P, Loiseau A, De La Chapelle M L, Lefrant S, Deniard P, Lee R and Fischer J E 1997 Large-scale production of single-walled carbon nanotubes by the electric-arc technique *Nature* 388 756–8
- [26] Iijima S 1991 Helical microtubules of graphitic carbon *Nature* 354 56–58
- [27] Yatom S, Selinsky R S, Koel B E and Raitses Y 2017 Synthesis-on" and "synthesis-off" modes of carbon arc operation during synthesis of carbon nanotubes *Carbon* 125 336–43
- [28] Keidar M and Waas A M 2004 On the conditions of carbon nanotube growth in the arc discharge *Nanotechnology* 15 1571
- [29] Journet C, Picher M and Jourdain V 2012 Carbon nanotube synthesis: from large-scale production to atom-by-atom growth *Nanotechnology* 23 142001
- [30] Cheung C L, Kurtz A, Park H and Lieber C M 2002 Diameter-controlled synthesis of carbon nanotubes J. Phys. Chem. B 106 2429–33
- [31] Nasibulin A G, Pikhitsa P V, Jiang H and Kauppinen E I 2005 Correlation between catalyst particle and single-walled carbon nanotube diameters *Carbon* 43 2251–7
- [32] Zhang X, Graves B, De Volder M, Yang W, Johnson T, Wen B, Su W, Nishida R, Xie S and Boies A 2020 High-precision solid catalysts for investigation of carbon nanotube synthesis and structure Sci. Adv. 6 eabb6010
- [33] Chen G, Seki Y, Kimura H, Sakurai S, Yumura M, Hata K and Futaba D N 2014 Diameter control of single-walled carbon

nanotube forests from 1.3–3.0 nm by arc plasma deposition *Sci. Rep.* **4** 3804

- [34] Johnson P L, Hanson R J, Carlos S and Taylor R W 2017 Plasma reactor US Patent 9,574,086 B2
- [35] Predtechenskiy 2020 Method and apparatus for producing carbon nanostructures US Patent 2020/0239316 A1
- [36] Dong X L, Zhang Z D, Xiao Q F, Zhao X G, Chuang Y C, Jin S R, Sun W M, Li Z J, Zheng Z X and Dong X L 1998 Characterization of ultrafine -Fe(C), -Fe(C) and Fe<sub>3</sub>C particles synthesized by arc-discharge in methane *J. Mater. Sci.* 33 1915–9
- [37] Hao C, Xiao F and Cui Z 2008 Preparation and structure of carbon encapsulated copper nanoparticles J. Nanopart. Res. 10 47–51
- [38] Zhang X, Rao Y, Guo J and Qin G 2016 Multiple-phase carbon-coated FeSn<sub>2</sub>/Sn nanocomposites for high-frequency microwave absorption *Carbon* 96 972–9
- [39] Sunny V, Sakthi Kumar D, Yoshida Y, Makarewicz M, Tabiś W and Anantharaman M R 2010 Synthesis and properties of highly stable nickel/carbon core/shell nanostructures Carbon 48 1643–51
- [40] Roy N C and Talukder M R 2018 Effect of pressure on the properties and species production in gliding arc Ar, O<sub>2</sub>, and air discharge plasmas *Phys. Plasmas* 25 093502
- [41] Syed B et al 2020 Effect of varying N2 pressure on DC arc plasma properties and microstructure of TiAlN coatings *Plasma Sources Sci. Technol.* 29 095015
- [42] Tanaka M, Tashiro S, Satoh T, Murphy A B and Lowke J J 2008 Influence of shielding gas composition on arc properties in TIG welding *Sci. Technol. Weld. Join.* 13 225–31
- [43] Gershman S and Raitses Y 2016 Unstable behavior of anodic arc discharge for synthesis of nanomaterials J. Phys. D: Appl. Phys. 49 345201
- [44] Liang F, Tanaka M, Choi S and Watanabe T 2017 Formation of different arc-anode attachment modes and their effect on temperature fluctuation for carbon nanomaterial production in DC arc discharge *Carbon* 117 100–11
- [45] Vekselman V, Feurer M, Huang T, Stratton B and Raitses Y 2017 Complex structure of the carbon arc discharge for synthesis of nanotubes *Plasma Sources Sci. Technol.* 26 065019
- [46] Khrabry A, Kaganovich I D, Khodak A, Vekselman V and Huang T 2020 Analytical model of low and high ablation regimes in carbon arcs J. Appl. Phys. 128 123303
- [47] Gutsch A, Mühlenweg H and Krämer M 2004 Tailor-made nanoparticles via gas-phase synthesis Small 1 30–46
- [48] Bokhonov B B 2014 Permeability of carbon shells during sulfidation of encapsulated silver nanoparticles *Carbon* 67 572–7
- [49] Zhang C et al 2018 Ethyne-reducing metal–organic frameworks to control fabrications of core/shell nanoparticles as catalysts ACS Catal. 8 7120–30
- [50] Wang C M, Baer D R, Thomas L E, Amonette J E, Antony J, Qiang Y and Duscher G 2005 Void formation during early stages of passivation: initial oxidation of iron nanoparticles at room temperature J. Appl. Phys. 98 094308
- [51] Diaz M C, Jiang H, Kauppinen E, Sharma R and Balbuena P B 2019 Can single-walled carbon nanotube diameter be defined by catalyst particle diameter? *J. Phys. Chem.* C 123 30305–17
- [52] Arora N and Sharma N N 2014 Arc discharge synthesis of carbon nanotubes: comprehensive review *Diam. Relat. Mater.* 50 135–50
- [53] Zhang D, Ye K, Yao Y, Liang F, Qu T, Ma W, Yang B, Dai Y and Watanabe T 2019 Controllable synthesis of carbon nanomaterials by direct current arc discharge from the inner wall of the chamber *Carbon* 142 278–84

- [54] Nemchinsky V A and Shigeta M 2012 Simple equations to describe aerosol growth *Modelling Simul. Mater. Sci. Eng.* 20 045017
- [55] Girshick S L and Chiu C 1990 Kinetic nucleation theory: a new expression for the rate of homogeneous nucleation from an ideal supersaturated vapor J. Chem. Phys. 93 1273–7
- [56] Lin M, Ying Tan J P, Boothroyd C, Loh K P, Tok E S and Foo Y-L 2006 Direct observation of single-walled carbon nanotube growth at the atomistic scale *Nano Lett.* 6 449–52
- [57] Ding F, Bolton K and Rosén A 2004 Nucleation and growth of single-walled carbon nanotubes: a molecular dynamics study J. Phys. Chem. B 108 17369–77