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*Review Article*

# Review of the Design and Operation Criteria of a DC Submerged Arc Discharge Carbon Nanostructure Synthesis Installation

**Lorenzo Hernandez-Tabares**,[1] **Frank J. Chao-Mujica**,[1] **Juan G. Darias-Gonzalez**,[1] **Luis M. Ledo Pereda**,[1] **Manuel Antuch**,[1] **Ernesto Carrillo-Barroso**,[2] **J. Enrique Chong-Quero**,[3] **and Luis F. Desdin-Garcia**[1]

[1]*Grupo de Nanociencia, Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear (CEADEN), La Habana 11300, Cuba*
[2]*Departamento de Física Aplicada, Instituto de Cibernética Matemática y Física (ICIMAF), La Habana 10400, Cuba*
[3]*Escuela de Ingeniería y Ciencias, Tecnologico de Monterrey, Monterrey, Edo. de Mex 52926, Mexico*

Correspondence should be addressed to Manuel Antuch; manuantcubi@yahoo.com, J. Enrique Chong-Quero; jchong@tec.mx and Luis F. Desdin-Garcia; desdin@ceaden.edu.cu

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The submerged arc discharge (SAD) allows the production of high-quality carbon nanostructures. The SAD method uses simple and inexpensive equipment. However, the carbon nanostructures obtained contain contaminants that are difficult to remove. The study of the published articles shows that reporting similar operating parameters informs quite different results. Reducing the generation of pollutants requires optimization of the design and the operation of installations. Nevertheless, the study of the state-of-the-art indicates that this aspect has been underestimated, which is manifested in the absence of publications on this subject. On the other hand, the increase in the production scale causes new problems that are not manifested in small-volume productions that are carried out in a research laboratory. The present work aims to analyze the SAD installation design and operation criteria to reduce the presence of contaminants. This study indicated that the key elements of the design and the operation are the electrodes alignment, feeding and attachment mechanisms, the electrode micropositioning system, the synthesis reactor design, the sensitive parameters control, the data acquisition system, and the selection of the liquid medium. Herein, these elements are analyzed and the best strategies for their design and operation are exposed. Those aspects relevant to scaling up of production are emphasized.

## 1. Introduction

Carbon is an exceptional chemical element. Owing to its capability to covalently bond with diverse orbital hybridizations, a prolific array of allotropes and molecular structures of several dimensionalities are shaped. For centuries, there were only two known pure carbon materials: diamond and graphite. In the latest decades, a series of new carbon allotropes with remarkable properties have been discovered [1]. Currently, carbon allotropes comprise a family that is the archetype of how the decrease of dimensions to the nanoscale leads to quantum confinement, and consequently to novel physical properties, beginning from electronics and optics, but also including thermal, mechanical, and chemical properties [2]. Multiple novel carbon nanomaterials have been created so far, which are investigated for numerous applications, ranging from energy harvesting, water treatment, biomedical devices, drug administration, building materials, electronics, and many more areas [3]. Currently, carbon nanomaterials are extensively employed in many products.

Among the new carbon allotropes, the MWCNTs occupy a remarkable place. The outstanding properties of MWCNTs have driven a new age of advanced multifunctional materials for a variety of applications such as polymer nanocomposites for structural applications, electrostatic discharge, and electromagnetic interference shielding applications, anode materials

for lithium-ion batteries, fuel cells, water purification, armor material, and conducting cables among other [3].

The most frequent MWCNTs production methods comprise the arc discharge in a gas environment, which demands a liquid-cooled hermetically sealed chamber with specific sliding or bellows seals for continuously cooled electrodes, complicated gas handling equipment, and time-spending purge cycles. After each limited production run, the chamber must be unsealed to extract the carbon soot containing the MWCNTs. Laser vaporization techniques suffer analogous constraints. The CVD processes require cumbersome gas handling systems and high-temperature furnaces [4].

The MWCNTs produced at a relatively low temperature tend to be very defective because carbon atoms deposited at the edge of the tubes do not have sufficient time to diffuse [5], creating defective edges with pentagons and heptagons, which will ultimately induce bending in nanotubes [6]. As a comparison, the MWCNTs manufactured using arc-discharged high-temperature procedure display a smaller amount of defects and lower resistivity [7]. At a minor temperature, the growth rate is also restricted owing to the diminished diffusion and reaction of carbons [8].

The arc discharge method is perhaps the most practical synthesis method. Some significant advantages can be enumerated in that respect such as fewer defects and high flexibility of MWCNTs manufactured, and minor emission capability degradation than those created by other methods [9].

While the abovementioned method can produce high-quality MWCNTs in yields appropriate for restricted research purposes, no method has been developed for the manufacture of high-quality MWCNTs adaptable to industrial production levels. Therefore, the optimization of the relationship quality–price remains a challenge.

The arc discharge was extended to liquid environments (SAD) to avoid the use of a vacuum system and gas control valves. The SAD is based on a short anodic arc with high anode ablation. In this method, the gap between the anode and the cathode is kept constant by shifting the anode relative to the immobile cathode as the anode ablates. This procedure is simple and able to yield high-quality MWCNTs. On the other hand, the SAD can run in a continuous form. At first, there was an overly optimistic view of this method. It was even stated that "… A most important feature of this new synthesis method is that there appear no obvious cost or technology obstacles to scale the method up for high-quantity production" [10] and in Biró et al.'s [11] study, it was concluded that SAD can be scaled up for industrial production levels. In Charinpanitkul et al.'s [12] study, it was asserted that "…it is widely recognized that arc-in-liquid method will be one of the most promising means for the actual industrial production of carbon nanoparticles." However, the MWCNTs via SAD are accompanied by other carbon nanostructures (CNSs) and impurities with alike structures. Hence, it is required laborious purification processes.

Quality carbon onions (CNOs) were found in floating materials shaped by SAD in water [13]. This discovery also contributed to a fast expansion of the SAD method given the simplicity of the experimental equipment [14]. Also in Wang et al.'s [15] study, it was reported the synthesis of single-wall carbon nanohorn (SWCNH) by SAD between two graphite electrodes in liquid nitrogen. Recently, in Chao-Mujica et al.'s [16] study, the synthesis of fluorescent CQDs and graphene oxide by SAD in water was reported.

The revision of state-of-the-art regarding SAD shows articles reporting similar operating parameters with quite different results. In most works, the electrode erosion rates are scarce and inconsistent, no rigorous CNSs yield values are reported and the CNSs purity degrees and the kind of contaminants present differ drastically. For instance, in numerous articles, it is affirmed that CNSs were obtained with high quality and purity. Nevertheless, many of these works do not carry out purification processes. These claims are based on SEM and TEM image analysis. SEM and TEM are valuable techniques, but their use for evaluation of bulk samples is questionable since less than 10–13 g of CNSs material per frame is observable and the CNSs soot is very heterogeneous.

From the previous analysis, it follows that to get a product with the maximum quality in the SAD, a thorough reduction of impurities is required. To achieve this purpose, several factors should be considered. One of them is a suitable design for the synthesis installation. Nevertheless, surprisingly the study of the SAD state-of-the-art shows that authors do not take into account this factor in their works. Therefore, the aim of the present work is to analyze the SAD design and operation criteria of the installations to manufacture high-quality CNSs.

## 2. Key Elements of the Design and Operation

Scaling up the production of CNSs by the SAD method requires careful design of the synthesis facility. This design must overcome the challenges imposed by the increase in the production volume that are not revealed in the synthesis on a laboratory scale for academic purposes. The design of manufacturing facilities for large production volumes and a high degree of operational flexibility is complex. This last element takes into account the possibility of using different types and dimensions of the electrodes, as well as the feasibility of carrying out the synthesis in liquid and gaseous media. It could also require work in a pulse regimen and in a wide range of powers. Nevertheless, the present study will be focused only on SAD with DC.

To identify the elements and to take into account in the design and operation, a study of the most cited publications on the subject was carried out. This study indicated that the key elements of the design (Figure 1) are the following: (1) electrodes alignment, feeding, and attachment mechanisms; (2) electrode micropositioning system; (3) synthesis reactor design; (4) sensitive parameters control; (5) data acquisition system; and (6) selection of the liquid medium.

In this section, we will analyze how these key elements have been addressed in the works published to date. Other important factors in the synthesis of CNSs are the quality of the electrodes and the discharge stabilization methods used. However, they are not the object of analysis of this work. The

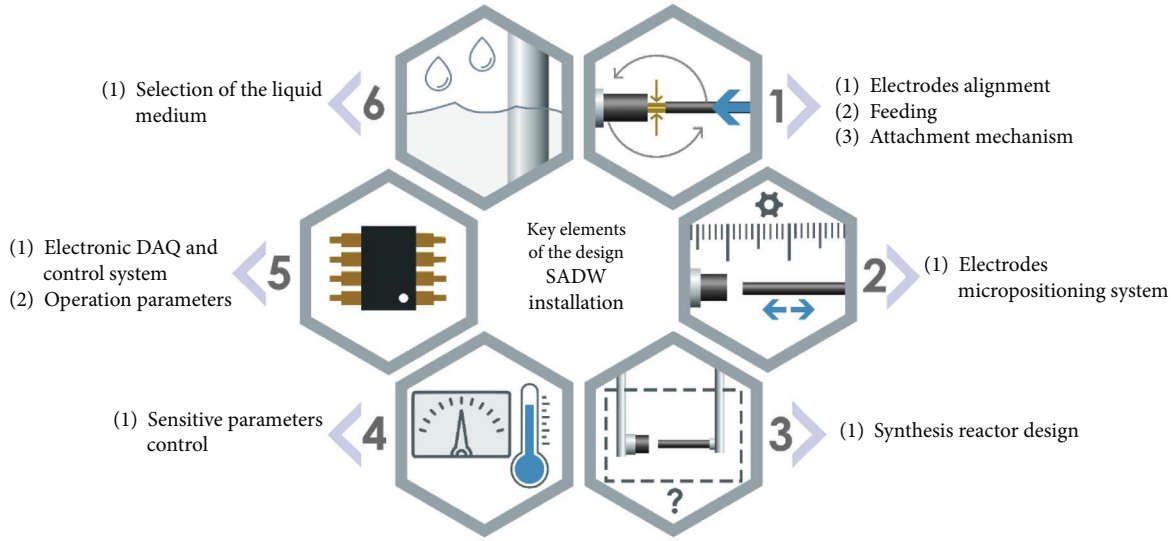


Figure 1: Key elements of the design of a SAD carbon nanostructures synthesis installation.

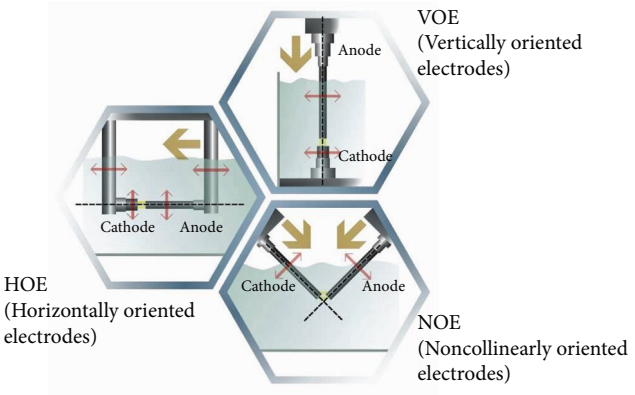


Figure 2: Scheme of the electrode alignment employed in the SAD.

features referring to the discharge stabilization methods were analyzed in detail [17].

## 3. Electrodes Alignment: Feeding and Attachment Mechanisms

The bibliographical study shows that the electrode feeding systems reported have different kinds of alignment (Figure 2, Table 1). In the great majority of the published articles, the electrodes were placed in a collinear way and with a horizontal orientation of the electrode (HOE). However, some of them have a vertical orientation of the electrodes (VOE). In Biró et al.'s [10] study, a simple apparatus for the synthesis of MWCNTs in liquid nitrogen was performed, using a VOE. In addition, single-walled carbon nanohorns using gas-injected arc in water have been investigated [18] using a VOE. Also, the development of an aqueous arc discharge set-up for 2D multilayered graphenes and 3D crumpled graphenes spheres synthesis was presented [19] with a VOE. Besides, in Li et al.'s [20] study, a water-protected arc discharge method was explained to manufacture MWCNTs with the same electrode orientation. Likewise, a discharge apparatus was assembled for the synthesis of carbon nanoonions (CNOs) [21] using a VOE.

In a reduced number of publications, a non-collinear alignment (NCA) was employed. In Kim et al.'s [22] study, a SAD method that comprises the use of physical vibration to the carbon electrodes with a NCA was studied. In addition, a simplified apparatus for producing carbon nanotubes using electrodes with different slant angles was revealed [23]. It is claimed in [11] a straightforward, low cost and continuous growth technique for the manufacture of well-graphitized MWCNTs with a NCA. SAD experiments were carried out between two graphite electrodes submerged in deionized water in a glass container. The angle between the electrodes was adjusted between 30° and 180° [24].

In the reported works, the feeding and attachment mechanisms are not described. However, this is a key element from the technological point of view. Increasing the production scale implies a frequent change of electrodes, so the installation must have a simple and easy replacement mechanism.

*3.1. Electrode Microposition System (EMS).* In the SAD to sustain a stable process at a certain power, the anode should be shifted with an appropriate velocity to compensate for the erosion (Table 2). The discharge in liquid is erratic; therefore, it is crucial to control accurately the arc gap to operate continuously. Most of the published studies operate in the 25–85 A range. In this range, the variation of the electrode erosion rate is significant. This demands from the EMS a smooth movement over a wide speed scale. The presence of vibrations in the EMS is detrimental. These produce electrical and thermal field oscillations in the gap, contributing to the heterogeneity of the manufactured nanostructures. They also lead to the detachment of particles from the electrode, contaminating the synthesis products. In most of the reported experiments, an EMS is not used and in many cases, the displacement of the electrodes is carried out manually. On

Table 1: Electrodes alignment and feeding and attachment mechanisms.

| Element | Recommendation |
|---|---|
| Alignment | Horizontal electrode alignment |
| Feeding | Able to use electrodes of different materials, lengths, and diameters |
| Attachment | Simple design and easy operation |
| Holder | Covered with an insulating material to prevent parasitic electrolysis |
| Fixing mechanism | Made of metal resistant to oxidation and thermal stress |

Table 2: Electrode micropositioning system requirements.

| Characteristics | Requirements |
|---|---|
| Velocity | Must be fine-tuned according to the arc power oscillations. The EMS must be able to work at very low speeds ($\sim\mu$m·s$^{-1}$) |
| Feedback | Current feedback is the most effective |
| Stabilization methods | The use of ballast resistors is recommended according to the synthesis current used |
| Displacement | Large—vibrations of the electrodes. Small—frequent replacement of electrodes |
| Scaling | At high current densities, the design and materials used are critical. Demands the choice of an optimal reactor volume. New difficulties are to be expected |
| Security | The EMS must have sensors that control the limits of its displacement. To avoid short circuits and mechanical damage |

the other hand, in those experiments in which it is used, no information is provided about the step motor and the sliding feeder arm employed.

In the literature, it can be appreciated that in the works that have used EMS, the values of the anode erosion rate vary considerably, even though in some cases, the power used is approximately the same. The anode erosion rate $R$ is quantified as the ratio of the difference between the starting and final mass of the anode and the total discharge time.

In Zhu et al.'s [23] study, it was reported that the total yield of nanotube-rich material was ~7 mg·min$^{-1}$ with 14 mg graphite consumed at 30 V and 50 A in water. The production rate of carbonaceous material was of the order of 5–10 mg·min$^{-1}$, in the case of the 85 A current in Biró et al.'s [11] study. The anode erosion in Sano et al.'s [25] study was approximately 117.2 mg·min$^{-1}$ with discharge voltage and current 16–17 V and 30 A, respectively. With an arc voltage and current of 34 V and 50 A, respectively, [15] the anode consumption rate was about 375.3 mg·min$^{-1}$ in liquid nitrogen. In Contini et al.'s [26] study, the experiments were performed with the anode moving toward the cathode at a steady speed of 11 mm·min$^{-1}$, while the cathode was rotating around its own axis at a speed of 30 rpm. The voltage range was 25–28 V and the corresponding current was in the range 50–80 A.

Details are not specified in most published works using EMS. Only in some works, a piece of brief information is offered [27, 28], since in them, the emphasis is on the structure and morphologies of the nanostructures obtained, as well as on the possible formation mechanisms.

*3.2. Synthesis Reactor.* The articles and available patent information show that up to now no attention has been paid to the design requirements of the reactor. Beakers of different volumes have been used as reactors [29]. In several cases, flammable organic solvents have been used without providing information on the engineering measures adopted [30]. In these open geometry experiments, the transport of the nanostructures carried by the gases generated in the convection processes is not controlled. As in many cases, the synthesis processes have been limited to periods of less than 2 min; cooling systems have not been required nor has any analysis been carried out on the aspects of the risks of extraction of the synthesized materials from the point of view of nanosecurity. Many of the reactor design aspects that have been underestimated in research work represent major challenges to scaling up the production.

*3.3. Sensitive Parameters.* The operation of a production installation demands the use of sensors to control the parameters that influence the quality of the products. The temperature must be monitored to avoid liquid loss and boiling. In some works, it is reported that the temperature of the liquid influences the production of nanoparticles [18]. The SAD is an intense source of sounds. The emitted sounds have a complex nature. They cannot be used as feedback to control the stability of the arc. However, the acoustic emission and its correlation with other parameters give valuable information concerning the operation of the installation. The emission of light in the SAD is not an appropriate parameter for the arc discharge control [31]. Nevertheless, it is a useful source of information on the environment in which the nanostructures are formed. Another parameter that is necessary to control is the level of the liquid. This aspect is of special importance in the case of the cryogenic liquids.

## 4. Electronic DAQ and Control System: Operation Parameters

The analysis of the state-of-the-art indicates that a production system of CNSs based on SAD needs a MPS controlled

by a feedback arc current measurement and a data acquisition system (DAQ) to record the relevant physical parameters in a correlated way. This approach was adopted in several investigations in gas discharges for CNSs synthesis [32].

The ablation of the graphite anode governs the synthesis yield of CNSs. For a great synthesis yield, the arc must work in a high ablation mode (current densities $> 100\,A \cdot cm^{-2}$) [33]. For currents greater than 55 A, part of the eroded material from the anode is deposited on the tip of the cathode. The amount of this material grows with increasing current. The deposition of eroded material on the cathode tip and their etching was defined as an inconvenience when using DC power [11]. To avoid this trouble, the abovementioned article used an AC source. In this case, there is no product accumulated on the electrodes after the synthesis experiments. The deposit peels off the actual cathode in the next half cycle when the polarity of the electrodes is inverted. Based on this advantage, the authors asserted that the AC method is well-suited for continuous operation and automation.

*4.1. Work Liquids.* The choice of the working liquid is an important element for obtaining nanostructures with the desired size and morphology and yield. Most of the experimentation has been carried out in water [23]. However, other liquids have been used for the synthesis. Among them is the use of cryogenic liquids such as liquid nitrogen [34] and liquid argon [35]. In these cases, it is intended to achieve a high value of the temperature gradient.

In other works, saline solutions have been used. In some of them, the objective has been to decorate MWCNTs with metal nanoparticles [36]. While in others, they use them owing to their better cooling ability than deionized water and cheaper than liquid nitrogen and helium [37].

## 5. Discussion of Design and Operation Criteria

In the previous section, the fundamental elements to be taken into account in the installation design and operation were identified and examined how they have been addressed in the published articles. This section will proceed to analyze the aspects related to the design and operation to optimize the CNSs synthesis.

Published works on SAD show that graphite anode electrodes with a diameter of 6 mm have been used in most of them. So from now on, the analyses will be carried out based on this anode diameter. However, this does not limit the scope of the conclusions obtained.

*5.1. Considerations about the Electrodes Alignment and Feeding and Attachment Mechanisms.* The election of the orientation of the electrodes is not debated in the published articles and the authors never explained the reason for their choosing. However, the orientation has an important role in the operation of the installation.

A VOE has the inconvenience that the convective and fluctuating gas flow moves for the surface of the upper electrode. Therefore, during a time fraction, a gaseous atmosphere surrounds the electrode and during another time fraction, a liquid environment contains the electrode, producing strong temperature oscillations. If the upper electrode is the cathode, such oscillations generate strong electron emission fluctuations because the Richardson–Dushmann law governs this process [38]. In case, the superior electrode is the anode, the temperature oscillation affects the thermoionization process that is responsible for the nanostructure formation in the hissing arc region. Then, the synthesis parameters undergo an erratic behavior affecting the nanostructures characteristic reproducibility. On the other hand, a fraction of the produced nanostructures with high hydrophobicity adheres to the electrode holder and to other higher parts of the installation. This circumstance affects the yield and the operation nanosecurity of the installation. In the work [12], the synthesis of CNSs in liquid nitrogen was investigated. The authors found that the increase in current leads to a reduction in the production yield of CNPs. This reduction in yield could be partly due to the entrainment of the nanostructures by the gas stream that grows with the current rise.

The use of a NCA is motivated by the desire of controlling the selectivity of onions to nanotubes production. In Sano et al.'s [25] study, it was asserted that the manufacturing rate and the selectivity of onions to nanotubes can be regulated because the growth depends on the directionality at the nanostructure formation region caused by the ion current. Many authors have adopted this point of view. One possible way to achieve directional control is to use a NCA. As well, in the abovementioned article, it was proposed the selectivity control (MWCNTs/CNOs) through the selection of the ratio between anode and cathode diameters. However, Hernandez-Tabares et al.'s [39] study showed that it is only possible in the arc stable zones if the facilities design excluded the vibrations. Furthermore, in Zhu et al.'s [23] study, it was reported the use of electrodes with different slant angles. Nevertheless, no noticeable change was found in as-grown products. On the other hand, the use of NCA complicates the mechanical design significantly.

The elements previously considered show that the HOEs is the most appropriate because its design is simpler, the electrodes experience less temperature fluctuation, and are easier to replace. In addition, there are fewer product losses and it is safer from a nanosecurity point of view. In the reported applications of the SAD so far, it is not justified to use other types of alignment.

A flexible and multipurpose installation must be able to use electrodes of different materials, lengths, and diameters. The electrode fixing mechanism must be made of metal resistant to oxidation and thermal stress. Since these processes increase the resistance of the electrode holder–electrode contact. This interface experiences accelerated deterioration, being one of the most frequent sources of operational failures.

A feeding mechanism that allows the use of long electrodes reduces the frequency of electrode replacement. However, the use of long electrodes can maximize vibrations and increase the detachment of microparticles from the electrode. Therefore, the electrode effective length should be minimized. A good quality feeding mechanism should keep

Table 3: Reactor design requirements.

| Details | Considerations |
|---|---|
| Product handling | The natural separation of the products must be preserved. Easy extraction of products |
| Nanosecurity | Closed reactor. Design that prevents spills. Liquid trap that retains the nanostructures dragged by the reactor outlet gases. Easy evacuation and cleaning |
| Cooling | Reactor with double metal walls and coupled cooling unit. Cooling fluid circulates between the walls |
| Volume | Choosing volume is a compromise. A large volume guarantees a high heat capacity and less demand on the cooling unit but complicates purification. A small volume faces the opposite situation |
| Window | The reactor must have a transparent window to observe the discharge area and record videos |

the electrode-free length small and constant to reduce the presence of graphitic impurities in the synthesis products.

In the synthesis stations, the electrode holders are metallic to transmit the current to the electrode. It is therefore recommended that the part of these is not in contact with the electrodes be covered with an insulating material to prevent parasitic electrolysis. This is especially important when DAS is used for the decoration of CNSs.

*5.2. Electrode Micropositioning System Requirements.* In the SAD to sustain a stable process at a certain power, the anode should be moved with an appropriate velocity to compensate for the erosion. However, this speed must be fine-tuned according to the arc power oscillations. The discharge happens in a sequence of stable (SZs) and unstable zones (UZs) that generate homogeneous and heterogeneous nucleation processes, respectively. In the SZs, the discharge goes on by a steady evaporation process [40]. However, in the UZs, the microposition system velocity is greater and the steps are more numerous. In each step, the gap fluctuates; therefore, the intensity of the electric field and, subsequently, the gas ionization also vary. Each step generates vibrations in the system that produce anode mass loss by grains crumbling. In addition, the power oscillations originate strong thermal stress that produced the graphite delamination [41]. Despite the fact that most of the discharge elapses in (SZs) zones, the main fraction of anode erosion takes place in UZs [39].

On the other hand, the occurrence of vibrations demands electrodes with the greatest flexural strength. Certainly, an unstable discharge was observed when used low-grade electrodes and defects in the obtained MWCNTs [42]. When experimenting with high currents, the importance of the EMS design and electrode quality is critical because the steps will be more frequent. Thus, the EMS vibrations and the diverse quality of the electrodes used are in some measure in charge of the inconsistent results informed in the literature (size, morphology, impurities, and so on).

The velocities' interval in which the EMS has been operated is very wide, from 3 $\mu$ms$^{-1}$ at 30 A (662 W) [39] to 1,500 $\mu$m s$^{-1}$ at 80 A (3,200 W) [18]. A comparison shows that in the second work, the SAD power is roughly five times bigger than in the first one, but the anode erosion rate is approximately 750 higher. The CNSs are formed by the carbon vapor's condensation, while the pollutants (mainly graphite microparticles) are created by anode pulverization. A simple assessment shows that if all electron beam power is employed in carbon sublimation, only this process can explain a little fraction of the eroded mass. This status quo is observed in many works. At the high speed of the EMS, the effect of arc discharge is essentially the pulverization of the anode.

To reach a soft and quiet sublimation process in the SAD, a high-quality EMS is necessary but not sufficient. The arc instability, the cause of micrographite particles and other contaminants, is an electromechanical phenomenon. Therefore, the mechanical design must be complemented by a suitable arc stabilization method because the EMS is not fast enough to adjust the arc gap to compensate for the arc power fluctuations. In Hernandez-tabares et al.'s [17] study, an analysis of different arc control strategies was performed. In the abovementioned, article was recommended a current control method complemented with the use of a ballast resistor.

Another aspect that will be kept in mind is the following one. The EMS must have sensors that control the limits of its displacement to avoid a short circuit between the cathode and the anode electrode holder when it wears out completely. In addition, the maximum displacement in the opposite direction should be limited after the synthesis to avoid mechanical damage to the EMS.

Large-scale production is only possible with the use of an EMS. However, its use causes other types of complexities in the synthesis. Such problems have not yet been examined.

*5.3. Reactor Design Requirements.* A natural phase separation occurs in the DAS. These phases are enriched in one or another kind of nanostructure. The supernatant is enriched in CNOs [43] and the residual water contains suspended materials: graphene oxide (GO) and carbon quantum dots (CDs) [16]. The precipitate has a more complex composition that include MWCNTs, CNOs, graphene, macro- and nanographite particles, amorphous carbon, and so on. In TEM images of the precipitates are observed clusters of CNOs and MWCNTs bounded chemically [17], probably owing to the existence of oxygen and hydrogen in the nanostructure growth region as it was revealed in Lange et al.'s [44] study.

The natural separation of the phases facilitates the purification process. Therefore, the design of the installation must preserve this process (Table 3). The decantation of the supernatant must be carried out easily and safely. This contributes to the reduction of the risk of spillage and, consequently, to the release of the nanostructures.

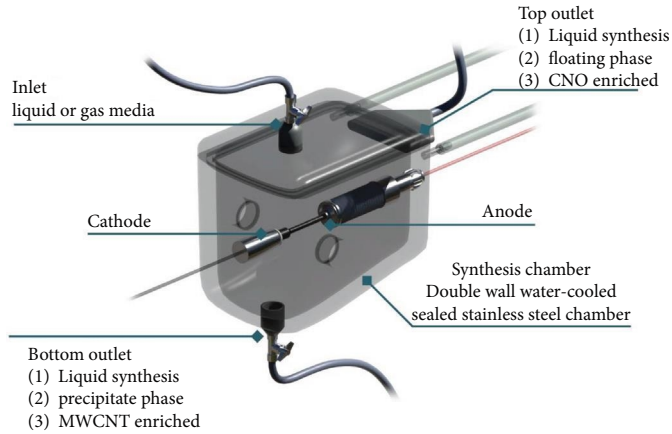


Figure 3: Nanostructure's extraction scheme in the SAD reactor.

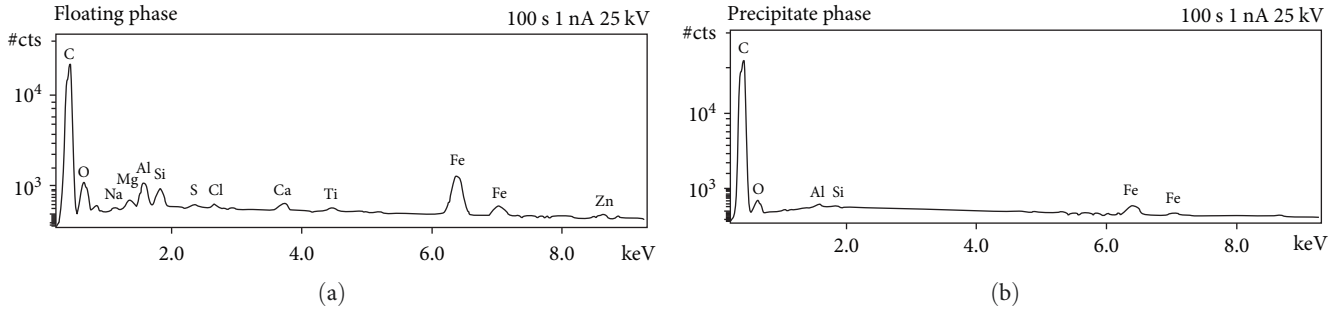


Figure 4: X-ray spectra of the supernatant sample (a) and precipitate (b) obtained using energy dispersive X-ray spectroscopy (EDX). (Published with the permission of the Revista Cubana de Física).

The nanostructures separation scheme is illustrated in Figure 3. The supernatant is extracted through pipeline 1 by adding water to the reactor volume. The bottom of the reactor is funnel shaped and sealed with a valve that opens to flush the precipitate from the vessel through pipeline 2. Finally, the suspension is obtained through pipeline 2 after concluding the collection of the precipitate. However, it will be necessary for any circumstance that the separated liquids remain at rest for no less than 24 hr to guarantee sedimentation, before undertaking other purification procedures.

A closed reactor offers greater versatility because it also allows making synthesis in a gassy atmosphere. In a closed design, it is possible to purge the air and substitute it with an inert gas. Therefore, it lets using flammable organic solvents as a liquid environment. In the SAD, powerful convection currents and a strong bubbling happen and they drag a fraction of the nanostructures generated in the synthesis region. These structures can be deposited in the installation's components and/or in the chemical hood where the synthesis is made, hindering the decontamination tasks. Therefore, the use of a closed reactor reduces the risk of nanostructures release.

In addition, in an open reactor, the chemical hood extraction transport contaminants, which are deposited in the supernatant. Therefore, contaminants concentration in the supernatant is higher than in the precipitate, as demonstrated in Darias et al.'s [45] study (Figure 4). A closed reactor excludes this problem.

The volume, geometry, and wall material election for the reactor influence its cooling efficiency. A bigger reactor volume helps to transfer heat from the arc region to the rest of the liquid through convective currents and has a greater surface of heat interchange. When the SAD is used to produce GO or CDs in water, they remain in suspension [16]. These nanostructures should be removed if the process is scaled up to make them more cost-effective and for nanosafety reasons [46]. However, a large volume of water makes the extraction process difficult and requires higher energy consumption. An alternative is to circulate and filter the liquid [47]. In this case, the benefit of natural phase's separation is lost.

A double metal wall reactor, with the circulation of cooling fluid between the inner and outer walls, guarantees a good heat exchange [47]. This design allows maintaining a low and constant temperature, minimizing the evaporation of the liquid, and keeping the height of the liquid column constant. These conditions ensure a stable bubble size, the true reactor in which nanostructures are created. Stable bubble size is a key condition for the reproducibility of the size and morphology of the produced nanostructures [48].

The gas evacuation system must include a liquid trap to retain the nanostructures carried by the gases generated. This is recommended from a nanosecurity point of view. Also, it would help to increase the performance of the synthesis because the nanostructures retained in the trap can be recovered. The exposure assessment of CNSs keeps on a challenge

Table 4: Control of sensitive parameters.

| Temporal evolution | Parameters | Importance of control |
|---|---|---|
| Slow changes | pH | It provides indirect information about the processes that occur and the stability of the colloid systems that arise |
| | Liquid temperature | A sufficiently low temperature prevents evaporation, provides a high liquid viscosity that increases vibration damping, and minimizes expansion of system components |
| | Liquid level | A constant water level in the reactor guarantees a constant pressure on the bubbles and a constant heat capacity. This contributes to the homogeneity of the characteristics of the CNSs |
| Fast changes | Sound emission | Contactless diagnosis. Vibrations of system components, bubble size, and chemical reactions present |
| | Light emission | Provides information about the environment of the discharge and in certain circumstances about the species present in it |

in the field of nanosecurity, as there have been relatively scarce sampling and monitoring investigations, and the sampling filters and methods have not yet been recognized. Direct reading devices for nanostructures counting and size distribution are incapable to represent CNSs correctly. Although several attempts have been completed to count the CNSs using TEM and other microscopic procedures, there are yet no standard methods for CNSs counting. Furthermore, determining the mass concentration of CNSs based on measuring the elemental carbon stays a defiance owing to the detection limits and complex character of existing analytical methods [49].

The reactor must be able to be easily cleaned and drained. It must also be able to be manipulated and removed from the rest of the synthesis station with minimal effort. It is recommended that the reactor have an appropriate window to be able to observe the discharge area during operation.

*5.4. Control of Sensitive Parameters.* The optimization of the synthesis and the correct operation of the installation requires the measurement of sensitive parameters. These are temperature, pH, liquid level, sound emission, and light emission (Table 4). The temperature, pH, and the level of the liquid vary slowly and do not need to be recorded in a correlated way with other parameters. Whereas light and sound emissions vary rapidly and are useful when recorded and correlated to current and voltage values. So that the design must contemplate the appropriate fixing elements for these sensors.

For the scaling of the process, it is important to have a cooling system that guarantees an adequate temperature to avoid the loss of liquid by evaporation. In addition, this process leads to a variation in the height of the liquid column and, consequently, in the pressure inside the bubbles that act as reactors where the formation of nanoparticles occurs. The variation in the size of the bubble alters the characteristics of the nanostructures, affecting the homogeneity of their dimensions and properties [48]. Guaranteeing a low temperature is also important when low boiling point liquids are used, especially when they are flammable. A low and stable temperature ensures a higher and constant viscosity, which results in greater damping of anode vibrations reducing crumbling. On the other hand, in some works, a great influence on the formation of nanostructures is attributed to the temperature gradient [18, 50]. Therefore, special measures are taken in these works to guarantee the desired temperature of the liquid. For these considerations, it is important to include in the design, a sensor of temperature with an automatic system of control of the same one.

It is recommended to provide the installation with a liquid level sensor with an automatic liquid replenishment system to compensate for losses due to evaporation [10]. This aspect is of special importance when cryogenic liquids with high currents are used.

With a view to better control the synthesis process, the use of optical and acoustic sensors is recommended. Therefore, in the design of the reactor, the possibility of appropriate fixation of these in an adequate position and distance must be considered. The spectrum of the sounds emitted in the SAD provides important clues about the operation of the installation. Sounds associated with the movement of mechanical elements such as electrodes, electrode holders, stepper motors, MPS elements, and bubbling have characteristic frequencies below 1 kHz. The processes associated with jet emission are in the range of several kilohertz. On the other hand, in the case of using water in which ions are present or in the case of using SAD to produce decorated structures, the emission spectrum can even extend up to hundreds of kilohertz.

Optical sensors provide information using emission spectroscopy. It allows for the estimation of the components of the plasma (H, O, C, $C_2$, etc.) and the temperature values in different regions of the arc [44].

## 6. Electronic DAQ and Control System Requirements: Operation Parameters Selection

The optimization of the SAD process requires the control of several parameters. Some of them have a slow variation, while others require a fast sampling rate. Among the former are the liquid temperature, pH, and level of the liquid. In the second group are the current, the voltage, the pulses of the stepper motor, the intensity of light emitted, the intensity of the sound, etc. (Table 5). The second group parameters require a high sampling rate and must be recorded in a correlated way. Their correlations provide valuable information on the

Table 5: Electronic DAQ and control system requirements, operation parameters selection.

| Measurements | Parameters | Observations |
|---|---|---|
| Correlated | Current | Optimal current density 106–177 A · cm$^{-2}$ (for typical anode $r = 0.3$ cm, $I$ in the range of 30–50 A). Source current range 0–70 A. The stabilization system must guarantee arc current fluctuations ≤3% |
| | Voltage | Source voltage range 0–70 V. The stabilization system must guarantee arc voltage fluctuations ≤5% |
| | Stepper motor pulses | The use of a step motor gave the possibility to know the anode displacement at any moment |
| | Light emission | Photodiode placed inside the reactor, in a plane perpendicular to the axis of the electrodes that intercepts it in the gap between them and coupled with optical fiber to the measurement system |
| | Sound emission | Contactless diagnosis. Detection of vibrations (electrode holders, electrodes, micropositioning system), bubbling, chemical reactions, and mechanical failures. It is recommended to use electret microphones because they are simple, robust, and cheap. Its frequency response is flat. The main SADW processes generate sounds with frequencies lower than 20 kHz. They are placed inside the reactor |
| Sampling rate | | >1,000 s−$^{1}$ |

processes that occur in the area where the nanostructures are synthesized.

In Hernández-Tabares et al.'s [51] study, it was reported a data acquisition system recorded five parameters in a correlated way with a sampling time of 50 s$^{-1}$. However, Gershman and Raitses [32] found the presence of processes with time scales of the order of $10^{-3}$ s. The authors discovered a correlation between current and voltage oscillations and the arc movement. Particularly, current and voltage measurements have shown nonstationary oscillations of current and voltage amplitudes, both at frequencies ∼200–300 Hz.

The analysis of the operating regimes indicates that the optimal region for production scaling using the SAD technique in the water is in the range of current $I$ from 30 to 50 A. If working at a value of $I$ is close to the critical (∼20 A), then the fluctuations can lead to a change from hissing to a silent regime. In the silent regime, field ionization acts and the yield of nanostructures formation is practically zero [52]. If working at currents greater than 50 A, the deposition of material on the cathode occurs. This process of growth of the end of the cathode by accretion modifies the gradients of the electric fields and the temperature of the synthesis region. In addition, at currents greater than 50 A, the thermal stress and vibrations of the anode lead to the detachment of the particles that make up the anode.

In Borgohain et al.'s [21] study, it was investigated the synthesis of CNOs prepared via SAD in water in the current range of 30–105 A. The products exhibited more graphitic impurities at higher currents, most likely due to mechanical fragmentation of the electrode.

Pure iron and graphite electrodes were utilized for CNSs by arc discharge in liquid nitrogen [12]. The products of the synthesis were MWCNTs, SWCNH, and carbon nanocapsules with core–shell structures. The CNSs yield synthesized by either carbon–carbon or carbon–iron electrodes became also lower with an increase in the current.

The previous information indicates the convenience of providing the installation with a DAQ with no less than five channels that allow recording the magnitudes sensed with a sampling of the order of 1 ms.

The control system must ensure the adequate displacement of the MPS in such a way that it compensates for the erosion of the anode at each moment in order to guarantee the value of the current selected for the synthesis. This system must operate in a wide MPS speed range 3–1,500 $\mu$m·s$^{-1}$. The experience reported in Hernández-Tabares et al.'s [51] suggested that the gap control software is of the "only forward" type. For large-scale production with a DAS installation, it is convenient for the system to have alarms that indicate the critical level of the liquid and the maximum permissible liquid temperature.

*6.1. Selection of Work Liquids.* The prevalent election of the liquid is deionized water [20, 22, 42] because of being economic and with a high heat capacity (Table 6). In this case, the reaction that is present in the interaction of the carbon vapors with the water is as follows:

$$\mathrm{C(s) + H_2O(l) \Delta \xrightarrow{\Delta} CO(g) + H_2(g).} \quad (1)$$

An intense bubbling is generated by the gases created in the reaction (1) and by the water vapor produced by the arc heating. When the bubble is attached to the electrodes, the nanostructures are formed inside of them. In the gas–liquid boundary exists a region in which a mutual diffusion between water molecules and carbon vapors, emitted gases, and dragged nanostructures is produced. This process drives nanostructures functionalization producing graphene oxide and carbon dots predominantly, which remain in suspension in the water. For that reason, special measures should be adopted to prevent the risk associated with suspension spilling and therefore the nanostructures liberation to the environment. One important element to take into account in the SAD is water purity. In the synthesis, the presence of parasitic electrolysis should be minimized. Parasitic electrolysis is a source of metallic contaminants observed in the products of synthesis. Some authors consider that these pollutants increase the nanotoxicity of the CNSs [53].

On the other hand, SAD is employed to decorate CNSs with metals. For this purpose, salts of these elements are added to the water. In such processes, electrolysis is strengthened by increasing oxygen production, thus rising carbon loss in CO emission and forming the chemical bonds between

Table 6: Selection of work liquids.

| Liquid | Advantages | Drawbacks |
|---|---|---|
| Water | Economic, high heat capacity, production of various types of nanostructures, natural phase separation | High carbon loss due to CO emission. High purity of water is required |
| Saline solution | Obtaining decorated nanostructures, better cooling, and better arc stability | Decorated particles are more toxic. Oxygen is emitted the bonds of which contribute to the agglutination of the CNSs |
| Cryogenic liquid | Obtaining unique exotic nanostructures (nanoflowers, nanoclusters, and nanohorns) | Expensive, strong bubbling that drags away CNSs (nanosafety risks), use of materials with a small thermal contraction coefficient |
| Organic solvents | The solvent is an additional source of carbon; when metal electrodes are used, core shell nanoparticles are obtained | Solvents carry the risk of being flammable and toxic |
| CNSs water suspension | Obtaining nanostructures decorated with metals with lower energy consumption because the power consumed in the discharge with metal electrodes is significantly lower than in graphite | Decorated particles are more toxic. Oxygen is emitted the bonds of which contribute to the agglutination of the CNSs |
| Water + organic solvents + surfactants | There is a very limited number of publications. Carbon sources increase. The authors claim an increase in CNSs yield. Reduction of fire risk | Purification problems, certain contaminants remain in suspension due to the action of surfactants |

MWCNTs and other CNSs and contaminants [24]. This could be the explanation why in Wang et al.'s [37], the precipitate fraction raised because the ether bridges joined MWCNTs, CNOs, and nanographite particles together. Furthermore, in the case of obtaining high-purity CNSs with the use of saline solutions, the purification procedures are problematic. It is necessary to eliminate the salt elements that are deposited on the surface of the CNSs. This can lead to the generation of defects in the nanostructures.

The nanostructures decoration happens in the above-mentioned gas–liquid interface region by heterogeneous nucleation. The atoms of the salts enter through diffusion to this region and are deposited on the surface of the nanostructures. This approach was used as a one-step synthesis route of carbon nanotubes decorated with palladium nanoparticles (~3 nm) [36].

The obtaining of decorated nanostructures has not always been the motivation to use saline solutions in SAD. In Montoro et al.'s [54] study, it was reported the utilization of $H_3VO_4$ aqueous solution in the SAD synthesis of SWCNTs and MWCNTs. The authors sustain that the choice of a vanadium compound was made based on its properties of promoting the formation of more ordered carbon structures. However, the presence of decorated nanostructures is not discussed. In some research, saline solutions were employed because of their better cooling ability than deionized water and more economical than liquid nitrogen and helium [37, 55]. In addition, the authors look for better arc stability increasing the liquid electric conductivity. However, to obtain pure CNSs, saline solutions should not be used due to the inevitable decoration effect that occurs.

The cooling capacity of sodium chloride solution is greater than that of deionized water. The maximum cooling rate of an 11 wt% NaCl solution is twice that of deionized water. Using a NaCl solution is significantly cheaper than using cryogenic liquids. Cryogenic liquids are used to achieve extreme quenching. The conductivity of water varies significantly with the addition of NaCl. For example, at 25°C, the electrical conductivity for concentrations of 0.025, 0.5, and 1 mol/L turns out to be 2,807.57, 31,677.92, and 37,242.09 $\mu$s/cm, respectively. Cryogenic liquids are considered electrical insulators. However, if they are heated to a high temperature, they will thermally ionize. A low-temperature plasma is present in the arc discharge channel in a cryogenic liquid, and plasma is electrically conductive. The aspects of cooling capacity and electrical conductivity are addressed in Wang et al.'s [37] and Jahanshahi et al.'s [55] studies.

Other liquids like LiCl solution [29], aqueous solutions of $Fe_2(SO_4)_3$ and $FeCl_3$ [56], and beer froth [57] have been used as an atmosphere in synthesizing CNTs using arc discharge.

In some works, the decoration is made by an inverse process [58]. For instance, for GO decoration, these nanostructures are dispersed in the liquid and are used with metal electrodes.

This approach is based on the fact that at the boundary between the GO suspension and the metal vapor zone, there is a mutual diffusion zone in which heterogeneous nucleation occurs. In it, the metal atoms nucleate on the GO platelet to form a nanostructure. As a result, GO platelets decorated with metals are generated. This approach has the advantage of consuming less energy because the current is much lower in the case of discharge between metal electrodes.

In the synthesis stations, the electrode holders are metallic in order to transmit the current to the electrode. It is therefore recommended that the part of these are not in contact with the electrodes be covered with an insulating material to prevent parasitic electrolysis. This is especially important when DAS is used for the decoration of CNSs.

A diversity of CNSs (MWCNTs, nanoflowers, nanoclusters, and nanohorns) could be made by SAD in cryogenic liquids [27, 59]. Using such liquids, no gas purging is necessary, as they offer a protective oxygen-free atmosphere as

well as being the source of the buffer gas in the course of the SAD. The use of cryogenic liquids guarantees a fast quenching required to obtain the previously mentioned CNS. The nanostructures synthesis has been reported using a wide range of currents, with so high values as 250 A [12]. When cryogenic liquids are used, it is necessary to guarantee a design and a selection of materials such that the contraction and expansion of the parts do not generate mechanical problems. This is of particular relevance to the MPS.

Organic solvents have also been used as an environment for SAD with the use of metallic electrodes. This is intended to use the solvent as a carbon source and the metal nanoparticles produced as a catalyst for the formation of nanostructures. In Okada et al.'s [30] study, obtaining MWCNTs in toluene using nickel electrodes was reported. This approach was also used in Liu and Meng's [60] study. These authors claim that onion-like fullerenes (OLFs) were produced by SAD in benzene using graphite as electrode and ferrocene as the catalyst. The use of water + organic solvent dispersions stabilized with the use of surfactants has also been reported. In Charinpanitkul et al.'s [61] study, the effect of monoolein surfactant, which promotes *n*-hexane to dissolve in water, was investigated to enhance the carbon nanoparticle (CNP) synthesis by SAD. The authors reported that an optimal amount of monoolein led to the maximal production rate of CNPs which was approximately two-fold higher than that obtained from a pure water system.

As a summary of the use of working liquids, it can be stated that deionized water is the most used liquid due to economic considerations and its high heat capacity that allows a good cooling process. The application of saline solutions is used to decorate the CNSs. But they are not justified to improve heat exchange if undecorated nanostructures are desired. Cryogenic liquids make manufacturing more expensive and are only justified when the objective is to obtain structures that can only be produced in the presence of extreme quenching. The use of organic solvents combined with metallic electrodes seems to be justified for the synthesis of core–shell structures with metallic nuclei. However, there is no evidence to indicate that they are more efficient than the use of deionized water for obtaining MWCNTs. Furthermore, these solvents carry the risk of being flammable and toxic. On the possible advantages and disadvantages of using suspensions of water with organic solvents stabilized with surfactants, there is still very little information available.

*6.2. Summary of Design and Operation Criteria.* The elements of design and operation of SADW facilities were previously discussed in detail. To facilitate the assimilation of the information provided, it is summarized in the form of tables.

## 7. Conclusions

Despite the large number of works reported on the use of DAS for the production of CNSs, it has not been possible to optimize this method. The products obtained present a great dispersion in their sizes and morphologies. In addition, they are obtained with a high level of contaminants that require complex purification processes.

In order to increase the yield and quality of the nanostructures manufactured by DAS, it is necessary to take into account several key elements that influence each other. Among those are as follows: (1) the stabilization of the discharge, (2) the use of electrodes of adequate quality, and (3) the improvement of the design and operation of the synthesis installation. Surprisingly, this last aspect has not been given much attention and its influence has been underestimated. On the other hand, the previous analysis suggests that the importance of the design and operation of synthesis facilities grows as the scale of production and the power used in its increase.

This study indicated that the crucial elements of the design and operation are the following: (1) electrodes alignment, feeding, and attachment mechanisms; (2) electrode micro-positioning system; (3) synthesis reactor design; (4) sensitive parameters control; (5) data acquisition system; and and (6) selection of the liquid medium.

The best way to place the electrodes is collinear with a horizontal orientation. The feeding and attachment mechanism must be able to use electrodes of different materials, lengths, and diameters. However, it should keep the electrode-free length small and constant to minimize the vibration.

The EMS must guarantee operation at a wide range of speeds with a minimum of vibrations at high arc powers. It must be built with materials that have small coefficients of expansion with temperature so that they can operate with different types of liquids and operating powers. The EMS must have sensors that control the limits of its displacement.

A closed-design reactor is more versatile and better from a nanosafety point of view. The design must preserve the spontaneous separation process that occurs in the synthesis and extraction of the products. The choice of its volume, geometry, and materials constitutes an optimization problem between the cooling efficiency and the volume of liquid to be handled to extract the products. A double metal wall reactor, with the circulation of cooling fluid between the inner and outer walls, guarantees a good heat exchange. The gas evacuation system must include a liquid trap to retain the nanostructures carried by the gases generated. The reactor must be able to be easily cleaned and drained. Also, it is recommended that the reactor has an appropriate window to observe the discharge area during operation.

The optimization of the synthesis and the correct operation of the installation requires the measurement of sensitive parameters. These are temperature, pH, and level of the liquid. The sound and light emissions provide useful information on the operation of the installation.

For the efficient operation of the installation, it is recommended that it has a multiparameter system that records in a correlated mode no less than five parameters with a sampling rate of $103\ s^{-1}$. The control system must guarantee the adequate displacement of the MPS in such a way that it compensates for the erosion of the anode at each moment in order to guarantee the value of the current selected for the synthesis. For large-scale production facilities, alarms indicating

the critical level of the liquid and the maximum permissible liquid temperature are recommended. The optimal current density range to operate an installation is between 106 and 177 $A \cdot cm^{-2}$ (30–50 A for a 6 mm diameter anode).

Deionized water is the most appropriate synthesis medium for the synthesis of nanostructures. Cryogenic liquids are expensive and are only justified when nanostructures are produced because of extreme quenching. Other liquids have a range of use limited to specific applications.

Facility designs and operating procedures must be analyzed using risk analysis tools to ensure they meet nanosafety requirements.

## Data Availability

The SAD nanostructure synthesis data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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