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Arc-Discharge Generation of Single-Wall Carbon Nanotubes and Aligned Ribbons using Ho/Ni Catalysts

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Abstract

This study explores the use of holmium (Ho) and nickel (Ni) as a novel bimetallic catalyst for synthesizing single-walled carbon nanotubes (SWNTs) using the arc discharge technique. By optimizing the concentration of Ho and Ni, long ribbons of SWNT bundles, with high purity and relatively narrow diameter distributions, were produced. The investigation demonstrates that while the Ho/Ni ratio does not significantly influence the SWNT diameter, it has a considerable effect on the yield and purity of the product. These findings suggest that the Ho/Ni catalyst combination is promising for the large-scale production of aligned SWNT assemblies, with potential applications in material science and nanotechnology.

Keywords: Carbon nanotubes, Holmium catalyst, Nickel catalyst, Arc discharge, SWNT ribbons, Raman spectroscopy

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1 Introduction

Single-walled carbon nanotubes (SWNTs) have garnered significant interest in the scientific and industrial communities due to their extraordinary physical, chemical, and electronic properties. SWNTs are cylindrical nanostructures composed of a single layer of carbon atoms arranged in a hexagonal lattice, which can exhibit metallic or semiconducting properties depending on their chirality and diameter [1]. These unique characteristics make them highly desirable for a wide range of applications, including materials reinforcement, nanoelectronics, sensors, energy storage devices, and biomedical applications. Their exceptional strength-to-weight ratio, high thermal and electrical conductivity, and large surface area make SWNTs a key material for the next generation of technological innovations [2].

SWNTs are often synthesized through various methods, including chemical vapor deposition (CVD), laser ablation, and arc discharge. Each method has its advantages and limitations, particularly in terms of scalability, purity, yield, and control over structural parameters such as diameter and chirality. Among these, the arc discharge technique has proven to be one of the most efficient for the large-scale production of SWNTs with high crystallinity. This method involves creating an electric arc between graphite electrodes in an inert gas atmosphere, which vaporizes the carbon and allows it to condense into nanotubes. Despite the advantages of the arc discharge method, controlling the yield, purity, and structural properties of the SWNTs remains a significant challenge. One of the most critical factors influencing these parameters is the choice of catalyst.

Catalysts play a vital role in the nucleation and growth of SWNTs. Initially, single transition metals, such as nickel (Ni), cobalt (Co), and iron (Fe), were used as catalysts for SWNT synthesis. These metals promote the decomposition of carbon-containing gases and the subsequent growth of nanotubes. However, research has shown that using bimetallic

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catalysts, particularly those composed of a transition metal combined with a rare-earth element, can enhance the efficiency of SWNT synthesis. For example, combinations like yttrium/nickel (Y/Ni), cerium/nickel (Ce/Ni), terbium/nickel (Tb/Ni), and lanthanum/nickel (La/Ni) have been studied extensively, demonstrating higher yields and improved control over the nanotube structure compared to single-metal catalysts [3].

The addition of rare-earth metals to transition metal catalysts has been found to influence the nanostructure of the SWNTs significantly. These metals can modify the surface energy and diffusion properties of the catalyst particles, which in turn affect the diameter, chirality, and yield of the resulting nanotubes [4]. For instance, Y/Ni has been reported to be one of the most effective catalysts for producing high-purity SWNTs, with diameters in the range of 1.2 to 1.6 nm. Similarly, Ce/Ni has been shown to yield SWNTs with smaller diameters, while Eu/Ni results in fewer nanotubes with a higher concentration of nanoparticles, indicating that the choice of rare-earth element can drastically alter the synthesis outcomes.

Despite the progress made in understanding the role of rare-earth elements in SWNT synthesis, there remain gaps in the knowledge regarding the catalytic mechanisms of different rare-earth metals. The exact function of these metals during the growth process is not entirely understood, though it has been proposed that the transition metal (such as Ni) primarily facilitates the carbon vapor's graphitization, while the rare-earth metal acts as a surfactant, controlling the size and composition of the catalyst particles. This hypothesis, however, requires further investigation, particularly with less-studied rare-earth metals such as holmium (Ho).

Holmium is a rare-earth metal that has not been widely explored in the context of SWNT synthesis. Its unique electronic structure and chemical properties suggest that it may offer similar, if not superior, catalytic capabilities when combined with nickel in a bimetallic system. Holmium has a high magnetic moment and stable oxidation states, which may influence the formation and growth of nanotubes in ways not observed with other rare-earth metals. Given the success of other rare-earth/nickel catalysts, it is worth investigating whether Ho/Ni can similarly produce SWNTs with high yield and purity, and whether this combination can provide additional benefits, such as enhanced control over the nanotube structure or the ability to form novel SWNT assemblies.

In addition to improving the yield and purity of SWNTs, researchers are also interested in developing methods for producing macroscopic assemblies of nanotubes, such as ribbons, fibers, and ropes. These assemblies consist of SWNT bundles that are relatively aligned, making them useful for applications in composites, micromechanical systems, and catalyst supports. Previous studies have demonstrated that modified arc discharge methods can produce such macroscopic assemblies, with varying degrees of success. For instance, Liu et al. synthesized ordered SWNT ropes using a sloped cathode in an H2/Ar atmosphere, while Gu et al. used Y/Ni with sulfur as a promoter to obtain SWNT fibers. More recently, methods like chemical vapor deposition (CVD) have been employed to directly spin SWNT fibers, producing long strands with potential for large-scale manufacturing [5].

This study aims to explore the potential of Ho/Ni as a catalyst for SWNT synthesis using a modified arc discharge method. In particular, it seeks to determine the effects of varying the Ho/Ni ratio on the yield, purity, and structural properties of the resulting SWNTs. Additionally, the study investigates the formation of long SWNT ribbons, a macroscopic assembly that could open new avenues for industrial applications. By systematically evaluating the catalyst's performance, this research contributes to the growing understanding of rare-earth/transition metal catalysts in SWNT synthesis and opens the door for further optimization of this promising material [1, 5, 6].

2 Experimental Procedure

The synthesis of single-walled carbon nanotubes (SWNTs) in this study was achieved using a modified arc discharge apparatus, a well-established method known for its effectiveness in producing high-purity SWNTs on a large scale. The arc discharge method involves vaporizing graphite in the presence of a catalyst using an electric arc generated between two electrodes. The precise control of experimental conditions, including the choice and ratio of catalysts, arc parameters, and atmospheric composition, is crucial for optimizing the yield, purity, and structural characteristics of the nanotubes produced.

2.1 Arc Discharge Apparatus Setup

The apparatus used for SWNT synthesis in this experiment was a conventional arc discharge system, with a few modifications aimed at enhancing the yield and purity of the nanotube product. The central component of the setup is a closed reaction chamber, which maintains a controlled environment for the arc discharge process. Inside the chamber, a direct current (DC) arc is generated between a graphite cathode and a movable graphite anode. The cathode was a solid graphite rod with a diameter of 8 mm, while the anode was also a graphite rod, spectrally pure, with an outer diameter of 6 mm and a length of 120 mm. A hole measuring 90 mm in length and 3 mm in diameter was drilled into the anode and filled with a catalyst mixture, as detailed in the following section.

To enhance the collection of the nanotube product, a hole with a diameter of 20 mm was drilled in the top of the reaction chamber. This hole was covered with a fine netting, which served as a collection point for the nanotube ribbons and other products formed during the arc discharge process. The netting facilitated the gathering of the lightweight and delicate SWNT ribbons, which are prone to adhere to surfaces due to their semi-transparent, sticky nature.

2.2 Catalyst Preparation

The choice of catalyst is one of the most critical factors influencing the synthesis of SWNTs. In this study, a bimetallic catalyst composed of holmium (Ho) and nickel (Ni) was used for the first time in the arc discharge process. The catalyst mixture was prepared by combining Ho2O3 (99.99% purity), Ni (99.99% purity), and graphite powder in varying ratios. The mixture was packed into the hole in the graphite anode, and the ratio of the Ho/Ni/graphite components was carefully controlled to investigate its effect on the yield and structure of the SWNTs.

The catalyst composition was expressed as Ho/Ni/C = n:m:(100 - n - m) atomic percent, where the holmium (Ho) content, n, ranged from 0.5% to 4%, and the nickel (Ni) content, m, ranged from 1% to 5%. The balance of the mixture consisted of graphite powder. This wide range of Ho and Ni concentrations allowed for a systematic study of the catalyst's influence on the properties of the SWNTs, including yield, purity, and diameter distribution.

2.3 Arc Discharge Process

The arc discharge process was conducted in a helium atmosphere, which provided an inert environment for nanotube formation while helping to maintain a stable arc. Helium gas, at a pressure of 600 Torr, was introduced into the reaction chamber. This pressure was selected based on previous studies showing that arc discharge in a helium atmosphere can produce nanotubes with high crystallinity and relatively uniform diameters.

A direct current of approximately 90 A and a voltage of 25 V were applied between the graphite anode and cathode. During the arc discharge process, a constant distance was maintained between the electrodes to ensure stable arcing conditions. The high current caused the graphite in the anode to vaporize, and the carbon atoms, along with the catalyst particles, condensed to form SWNTs.

One of the unique features of this experimental setup was the production of web-like and collar-like assemblies of SWNTs, similar to those produced in previous experiments using Y/Ni catalysts. In addition, semi-transparent SWNT ribbons, with lengths ranging from 10 to 20 cm, were obtained. These ribbons were collected on the netting placed over the hole in the reaction chamber. Due to their thin, sticky nature, the ribbons exhibited strong adhesion to collection tools like tweezers, making careful handling necessary during the collection process.

2.4 Sample Collection and Quantification

Following the arc discharge process, the total as-grown SWNT product was collected. This included the semi-transparent ribbons, as well as web-like soot and collar-like formations (collectively referred to as cathode soot) deposited near the cathode. In addition, chamber soot, which accumulated on the walls of the reaction chamber, was also collected. The cathode soot was typically found to contain a higher concentration of SWNTs, while the chamber soot was composed of a lower concentration of SWNTs, along with other carbonaceous materials.

The total weight of the collected products ranged from 0.6 to 1 g per run, depending on the catalyst composition and the duration of the arc discharge, which varied between 5 and 10 minutes. This relatively short production time reflects the high efficiency of the arc discharge method for generating SWNTs.

2.5 Characterization Techniques

The as-grown SWNT products were subjected to a variety of characterization techniques to assess their structural properties, yield, and purity. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to examine the morphology of the SWNT ribbons and bundles, providing detailed images of the nanotube structures. SEM allowed for the observation of large-scale features, such as the alignment and thickness of the SWNT ribbons, while TEM provided high-resolution images of the individual nanotubes within the bundles.

Thermogravimetric analysis (TGA) was employed to evaluate the thermal stability of the SWNT samples, as well as to estimate the relative purity of the nanotube product by comparing the oxidation temperatures of amorphous carbon and SWNTs. Raman spectroscopy, with excitation wavelengths of 488 nm, 514.5 nm, 632 nm, and 780 nm, was used to determine the diameter distribution of the SWNTs and to detect any defects or impurities in the samples. Additionally, UV-NIR spectroscopy was used to further assess the purity of the SWNTs by analyzing the absorption spectra of the samples in the near-infrared region.

2.6 Optimization of Catalyst Ratios

To determine the optimal conditions for SWNT synthesis, the Ho/Ni catalyst ratio was systematically varied. The yield of SWNT-containing products was calculated as the ratio of the weight of the cathode soot to the total weight of collected soot (including both cathode and chamber soot). This yield was then correlated with the purity and diameter distribution of the SWNTs, as determined by Raman spectroscopy and other characterization techniques.

3 Results and Discussion

The results of this study provide a comprehensive examination of the synthesis of single-walled carbon nanotubes (SWNTs) using holmium (Ho) and nickel (Ni) as catalysts in an arc discharge process. The findings demonstrate not only the effectiveness of this bimetallic catalyst combination but also offer insights into how varying the Ho/Ni ratio impacts the yield, purity, and structural characteristics of the SWNTs. In today's context, SWNT synthesis remains a critical area of research for applications in nanotechnology, materials science, and electronics. Therefore, this section will discuss the relevance of these results in light of contemporary advancements in the field.

3.1 Morphological Characterization of SWNTs

The use of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provided clear evidence of the successful synthesis of SWNTs using the Ho/Ni catalyst system [3, 7]. The as-grown products collected from the cathode and reaction chamber consisted of various morphologies, including web-like soot, collar-like assemblies, and notably, long SWNT ribbons. The semi-transparent ribbons, which reached lengths of 10 to 20 cm, were composed of roughly aligned SWNT bundles, with diameters estimated between 10 and 30 nm.

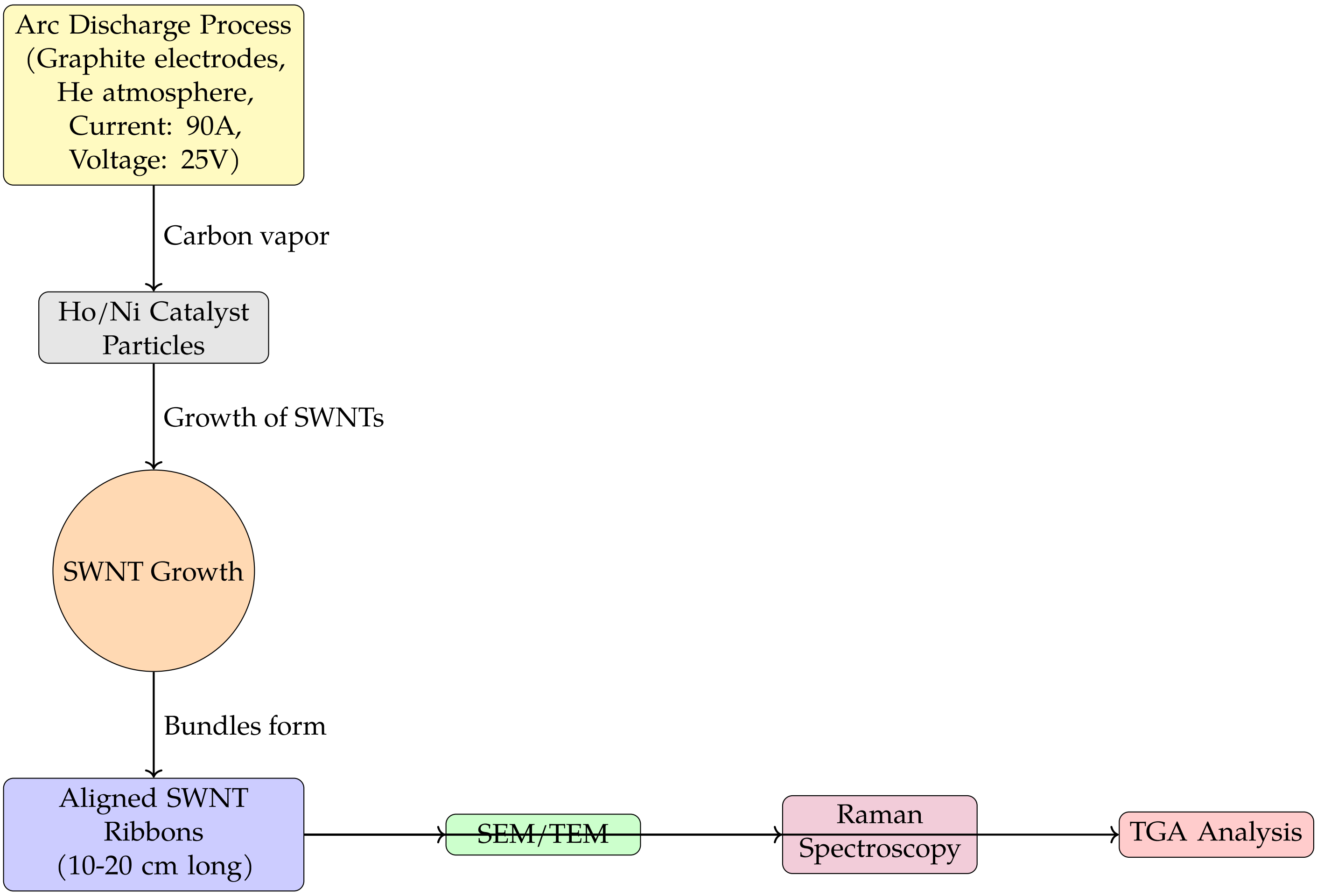
High-resolution TEM images revealed that the SWNT ribbons were composed of bundles of well-aligned nanotubes, confirming their high structural quality. Few defects were observed, and the nanotubes within the bundles were tightly packed, suggesting that the Ho/Ni catalyst system facilitates the formation of highly ordered nanotube structures. This is particularly important in modern applications, as the alignment and purity of SWNTs directly influence their electronic, mechanical, and optical properties.

In comparison to earlier studies using other rare-earth catalysts, such as Y/Ni or Ce/Ni, the Ho/Ni catalyst produced SWNTs with comparable or superior alignment and purity. This suggests that holmium, which has not been extensively studied in this context, is an effective co-catalyst when paired with nickel, contributing to the growth of high-quality SWNTs. In today's landscape, where the demand for scalable production of defect-free SWNTs for use in flexible electronics, sensors, and composite materials is rising, the ability to produce such highly aligned structures is a significant advantage [4].

3.2 Thermogravimetric Analysis (TGA) and Purity Evaluation

Thermogravimetric analysis (TGA) was performed to assess the thermal stability and relative purity of the SWNT products. By ramping the temperature from 30°C to 900°C at a rate of 5°C per minute in an air atmosphere, the oxidation behavior of the SWNTs and any amorphous carbon impurities was measured. TGA curves for the as-grown samples demonstrated a distinct difference between the ribbon-like and collar-like products, with the SWNT ribbons exhibiting less amorphous carbon content [8].

The oxidation temperature of amorphous carbon is generally lower than that of SWNTs, with the TGA curve for the ribbons showing a reduced intensity of the derivative thermogravimetry (DTG) peak around 380°C, corresponding to amorphous carbon oxidation, and a higher peak near 430°C, associated with the oxidation of SWNTs. This indicates that the SWNT ribbons contain a higher purity of nanotubes compared to the collar-like products. The residues remaining at 900°C were found to be mainly oxidized catalyst


Arc Discharge Process (Graphite electrodes, He atmosphere, Current: 90A, Voltage: 25V)
Carbon vapor
Ho/Ni Catalyst Particles
Growth of SWNTs
SWNT Growth
Bundles form
Aligned SWNT Ribbons (10-20 cm long)
SEM/TEM
Raman Spectroscopy
TGA Analysis

particles, which further corroborates the high purity of the ribbons.

In modern applications [9], high-purity SWNTs are critical for the efficient performance of nanoelectronics and other advanced materials. Impurities, such as amorphous carbon, can interfere with the electrical properties of SWNTs, reducing their conductivity and performance. Thus, the findings of this study, which demonstrate that the Ho/Ni catalyst system produces SWNT ribbons with minimal impurities, are highly relevant to contemporary research, where purity is often a primary concern.

3.3 Raman Spectroscopy and Diameter Distribution

Raman spectroscopy was employed to further characterize the as-grown SWNT samples, with particular attention paid to the diameter distribution and the presence of defects or impurities. Raman spectra of the SWNT ribbons exhibited characteristic features, such as the radial breathing modes (RBM) in the 140–190 cm-1 region and tangential modes (G band) near 1590 cm-1. These features confirmed the presence of SWNTs in the samples. The G band's high intensity, coupled with the low intensity of the disorder-induced D band near 1300 cm-1, indicated a low level of defects in the SWNTs, which is consistent with the findings from TGA and SEM analyses.

Using four different laser excitation wavelengths (488, 514.5, 632, and 780 nm), the Raman spectra provided information about the diameter distribution of the SWNTs. The RBM frequencies corresponded to SWNT diameters ranging from 1.3 to 1.7 nm, which is a relatively narrow distribution compared to other catalyst systems. This narrow diameter distribution is desirable in modern applications, particularly in nanoelectronics, where the electronic properties of SWNTs are diameter-dependent. The ability to control SWNT diameters through the choice of catalyst is a crucial advancement in ensuring the reproducibility and functionality of SWNT-based devices [10].

In today's research on SWNTs, controlling the diameter and chirality remains a significant challenge. The Ho/Ni catalyst system's ability to produce SWNTs with a consistent diameter distribution adds value, especially in applications such as transistors, where semiconducting SWNTs are preferred, and in composite materials, where uniformity in nanotube size contributes to more predictable mechanical properties.

3.4 Optimization of Ho/Ni Catalyst Ratios

One of the critical findings of this study is the optimization of the Ho/Ni catalyst ratio for maximizing the yield and purity of SWNTs. By systematically varying the concentration of Ho (0.5%–4%) and Ni (1%–5%), the study found that the optimal range for producing high-purity, high-yield SWNTs was when the Ho concentration was between 1% and 2%, and the Ni concentration was maintained at 2% [11]. At these concentrations, the SWNT ribbons were produced with the highest yield and lowest defect density, as confirmed by Raman spectroscopy and UV-NIR absorption measurements.

The study's optimization approach is highly relevant in today's research, where fine-tuning catalyst composition is crucial for the large-scale, cost-effective production of SWNTs. In industrial contexts, the ability to produce SWNTs with high yield and purity without complex purification steps reduces production costs and increases the feasibility of using SWNTs in commercial applications, such as in energy storage, flexible displays, and conductive films.

UV-NIR spectroscopy was employed to further quantify the purity of the SWNTs. The ratio of the spectral area of the second transition band in the near-infrared region (7750–11750 cm-1) to the total spectral area provided a relative measure of SWNT purity. The highest relative purity (RP) values were observed for SWNTs synthesized with a Ho/Ni ratio of 1:2 or 1:3, with RP values reaching up to 69%. These results are comparable to those obtained with Y/Ni catalysts, which have been among the most effective systems studied to date.

In modern applications, especially in electronics, high-purity SWNTs are essential for minimizing electrical resistance and maximizing device performance. The ability of the Ho/Ni catalyst system to produce SWNTs with comparable purity to well-established systems like Y/Ni is significant, as it offers a new avenue for catalyst selection in SWNT production. Moreover, holmium, being less explored than yttrium, presents an opportunity for further investigation into rare-earth catalysts that could offer cost or performance benefits.

The results of this study highlight the potential of Ho/Ni as an effective catalyst for the production of high-purity, well-aligned SWNTs with a narrow diameter distribution. In today's context, where SWNTs are being developed for a broad range of applications—from next-generation transistors and sensors to energy storage and reinforcement in composite materials—the ability to synthesize high-quality SWNTs at scale is critical.

Moreover, the formation of long SWNT ribbons, as demonstrated in this study, holds promise for applications requiring macroscopic assemblies of nanotubes. Such ribbons could be integrated into flexible, lightweight materials for aerospace and automotive industries or used as scaffolds for growing other nanomaterials in advanced manufacturing processes.

4 Conclusion

This study demonstrates the successful synthesis of single-walled carbon nanotubes (SWNTs) using a novel bimetallic catalyst composed of holmium (Ho) and nickel (Ni) through a modified arc discharge method. The results show that both Ho and Ni play essential roles in producing SWNTs with high yield and purity, as well as enabling the formation of long, aligned SWNT ribbons. The Ho/Ni catalyst system was found to be highly effective in controlling the nanotube morphology, with varying concentrations of Ho and Ni significantly influencing the yield and structural characteristics of the SWNTs without notably affecting their diameter distribution.

Through extensive characterization using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and thermogravimetric analysis (TGA), the study found that the optimal Ho/Ni ratio for maximizing yield and purity falls within a narrow range, with a Ho concentration between 1% and 2% and a Ni concentration at 2%. This optimal composition produced SWNT ribbons with relatively high purity, minimal defects, and consistent diameters ranging from 1.3 to 1.7 nm. The findings also revealed that the Ho/Ni catalyst performs comparably to other rare-earth/transition metal combinations, such as Y/Ni, which are widely regarded as among the most effective catalysts for SWNT synthesis.

References

[1] Szabó, Andrea, et al. "Synthesis methods of carbon nanotubes and related materials." Materials 3.5 (2010): 3092-3140.

[2] Mevellec, J. Y., et al. "M. Baibarac, L. Mihut, N. Preda, I. Baltog."

[3] Saxena, Swasti, and Ankit Kumar Srivastava. "Carbon nanotube-based sensors and their application." Nano-Optics. Elsevier, 2020. 265-291.

[4] Ling, Xin-Long, et al. "Preparation and characterization of hydroxylated multi-walled carbon nanotubes." Colloids and Surfaces A: Physicochemical and Engineering Aspects 421 (2013): 9-15.

[5] Fialkova, Svitlana. "Application of Nano-Imprint Lithography for Next Generation Carbon Nanotube-Based Devices." (2013).

[6] Khataee, A. R., et al. "Environmental applications of activated carbon and carbon nanotubes." Chemical Physics Research Journal 4.3/4 (2011): 167.

[7] Wang, Wenhu. "Hierarchical Hybrid Materials from Flexible Fabric Substrates." (2020).

[8] Perri, Caterina, Raffaele Molinari, and Jànos B. Nagy. "Nanotubi di carbonio multiparete: ottimizzazione dei parametri di sintesi per la produzione su larga scala." (2010).

[9] Keidar, Michael. "Factors affecting synthesis of single wall carbon nanotubes in arc discharge." Journal of Physics D: Applied Physics 40.8 (2007): 2388.

[10] Fang, Xiuqi, et al. "Determining synthesis region of the single wall carbon nanotubes in arc plasma volume." Carbon 107 (2016): 273-280.

[11] Keidar, Michael, et al. "Magnetic-field-enhanced synthesis of single-wall carbon nanotubes in arc discharge." Journal of Applied Physics 103.9 (2008).