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LOW-TEMPERATURE GROWTH OF CARBON NANOTUBES USING NICKEL CATALYST

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This study presents the results of a comprehensive investigation into the fabrication of single-walled carbon nanotubes (SWCNTs) employing chemical vapor deposition (CVD) technique, with nickel nanoparticles serving as crucial catalysts. These nanoparticles are synthesized via the reduction of oxide precursors using hydrogen and are strategically incorporated with ethanol vapor as the primary carbon source. The effectiveness and reproducibility of this synthesis method are thoroughly validated using advanced analytical techniques. Particularly noteworthy is the demonstrated ability to conduct the process at relatively low temperatures, not exceeding 500°C, which is of significant importance. Such precise control over synthesis conditions not only augurs well for the scalability of SWCNT production but also carries substantial implications for the advancement of nanomaterial synthesis methodologies.
Keywords: *Catalysts, Single-walled carbon nanotubes, Multi-walled carbon nanotubes, X-ray phase analysis, Light scattering spectroscopy, Scanning electron microscopy*
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INTRODUCTION

Carbon nanotubes (CNTs) possess exceptional electrical and thermal conductivity alongside remarkable strength and durability [1]. These properties render them valuable across various fields such as energy storage [2-3], construction materials [4], chip technology [5], biomedical applications [6], and increasingly, electronic microcircuits due to their high electrical conductivity [7]. CNTs, essentially seamless cylinders comprised of rolled-up graphene sheets, exist in two primary forms: single-walled and multi-walled. Single-walled CNTs have diameters ranging from 0.4 to 4 nm, while multi-walled CNTs consist of several concentric shells of single-walled tubes with diameters ranging from 1.4 to 100 nm and a wall-to-wall distance of 0.34 nm [8].

Since their discovery, methods for synthesizing CNTs have garnered increasing interest [9], including arc discharge, laser ablation, chemical vapor deposition (CVD), and plasma-enhanced chemical vapor deposition (PECVD). Among these methods, CVD stands out for its cost-effectiveness, scalability, and widespread adoption. The quality of CNTs synthesized via CVD depends on various parameters such as catalyst type, substrate, carbon source, reaction conditions (time and temperature), gas flow rate, and specific surface area of the resulting powder [10]. Additionally, the diameter of CNTs obtained via CVD is influenced by the catalyst type, with commonly used catalysts including Fe, Ni, Co, and their alloys. Studies have shown that pure nickel and cobalt exhibit higher catalytic activity compared to iron [11].

For instance, in [12], CNTs were synthesized from ethanol at 1150°C using catalysts from the VIII group (Fe, Co, Ni) based on corresponding metallocenes. Employment of trimetallic catalysts notably enhanced CNT yield, although mixtures of two or three metallocenes as catalysts led to increased structural defects in CNTs. In another study [13], multi-walled CNTs were synthesized on a silicon substrate via CVD using ethanol at 800°C with three different metallic catalysts (iron, copper, and nickel). Moreover, [14] observed improved CNT quality with a gradual temperature increase from 500°C to 650°C, but further temperature elevation hindered CNT formation, attributed to nickel particle enlargement at higher temperatures.

In summary, relatively few studies have investigated CVD synthesis of CNTs using nickel as a catalyst at low temperatures. Our work addresses this gap, presenting results from CVD synthesis of single-walled CNTs utilizing a nickel catalyst at relatively low process temperatures.

The CVD method is widely employed for synthesizing CNTs. In this process, a gas mixture containing carbon source materials (such as methane, ethylene, or acetylene) is introduced into a reactor, where it reacts with a heated substrate coated with a catalyst. Carbon atoms then condense on the substrate's surface, sequentially adding to the growing nanotube, thereby controlling its structure and properties, including length, diameter, orientation, and efficiency.

EXPERIMENTAL PROCEDURE

In our experiments, pairs of ethanol vapor with a purity of 96.5% served as the hydrocarbon source. Nickel nanoparticles, obtained through the hydrogen reduction of nickel oxide synthesized via the sol-gel method, were utilized as the catalyst. Upon obtaining nickel nanoparticles, hydrogen supply to the reactor was halted, and the temperature was elevated to 500°C to initiate the synthesis of carbon nanotubes (CNTs). Ethanol vapor was introduced into the reactor

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using Ar as the carrier gas at a flow rate of 5 l/min. The CNT synthesis process lasted approximately 30 minutes, during which side products resulting from pyrolysis were eliminated through combustion. The characteristics of the synthesized CNTs were examined utilizing scanning electron microscopy (SEM), X-ray structural analysis (XRD), and energy-dispersive X-ray spectroscopy (EDX) techniques employing state-of-the-art, metrologically certified equipment.

RESULTS AND DISCUSSION

Figure 1 displays an image acquired through scanning electron microscopy, illustrating a cluster of single-walled carbon nanotubes synthesized under the described conditions. The resultant product manifested as spiderweb-like fibers, predominantly aggregating at the bottom of the reactor. Analysis of the product revealed its composition to comprise fibrous carbon with traces of nickel and oxygen, devoid of any other impurities.

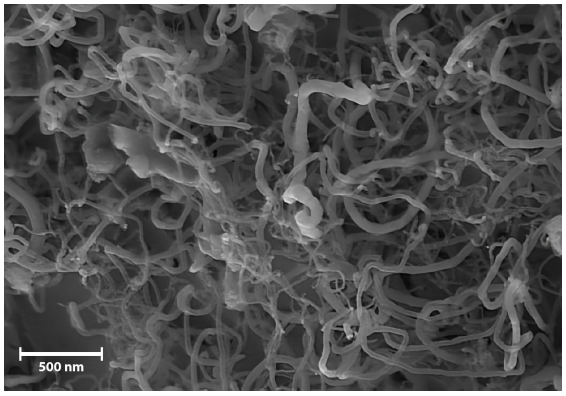

Figure 1. SEM image of a group of carbon nanotubes.

Additionally, a portion of the product deposited as wall-like formations exhibiting similar morphology and purity. The elemental composition of the nanotubes was determined through EDX analysis, with the results depicted in Figure 2. The analysis revealed that over 94% of the carbon nanotubes are composed of carbon.

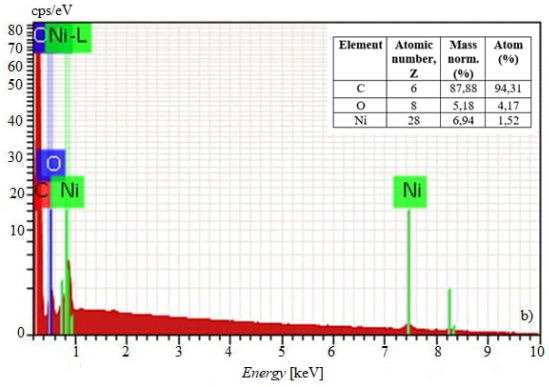

Figure 2. Results of energy-dispersive X-ray (EDX) analysis illustrating the composition of carbon nanotubes synthesized via the chemical vapor deposition (CVD) method

The elemental composition of the nanotubes was determined by EDX analysis (Bruker, SDD, XFlash 6/60, Berlin, Germany), the results of which are presented. It can be seen that more than 94% of the CNTs consist of carbon.

Raman spectroscopy studies were performed using equipment produced by "Renishaw", United Kingdom. A "green" laser with a wavelength of 532 nm and a nominal power of 100 mW was selected for measurement. Measurements were carried out in the wavenumber range from 100 to 3200 cm^{-1}. The signal acquisition time was 10 seconds. The results are shown in Figure 3.

The radial breathing mode (RBM) peak exclusively manifests in single-walled carbon nanotubes (SWCNTs), within the frequency spectrum ranging from 100 to 500 cm^{-1}. This peak's position is inversely correlated with the diameter of the nanotube and can be determined by the following Equation (1).

$$\omega_{RBM} = A/(dt) + B\,, \tag{1}$$

where, ω_{RBM} represents the oscillation frequency, while A and B are constants, and dt denotes the diameter of the carbon nanotube (CNT).

The observation of the characteristic peak, namely the radial breathing mode (RBM) peak, at a frequency of 121 cm^{-1} indicates the successful synthesis of single-walled CNTs using nickel as a catalyst via the chemical vapor deposition

(CVD) method. Based on this result, it can be inferred that the diameter of the single-walled CNTs synthesized, as determined by Equation (1), is approximately ~2 nm.

Furthermore, the D peak, indicative of defects in the CNTs, as shown in Figure 3, is measured at 1341 cm^{-1}. Additionally, the G peak, primarily describing the C-C bond and deformation in CNTs, registers at 1568 cm^{-1}. The G' peak, which characterizes doping and isotopic features in CNTs, corresponds to 2683 cm^{-1}. The quality assessment of synthesized CNTs is commonly evaluated by the ratio of the intensity of the D peak (I_D) to the intensity of the G peak (I_G), denoted as (I_D/I_G). In this case, the calculated ratio is 0.5, indicating qualitative adherence to the definition of this parameter.

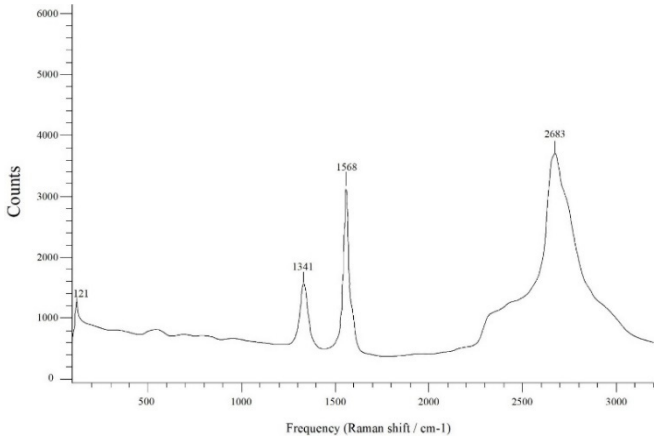

Figure 3. Raman spectra of carbon nanotubes synthesized by the CVD method

Figure 4 presents X-ray diffraction (XRD) patterns of carbon nanotubes. XRD, a rapid analysis technique, is utilized for material identification, notable for its capacity to evaluate both local and overall material characteristics, encompassing lattice structure with phase morphology [15], interlayer distances, among others.

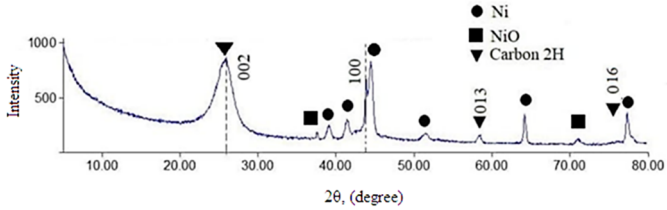

Figure 4. X-ray diffraction (XRD) patterns of carbon nanotubes synthesized by the CVD method

Figure 4 presents X-ray diffraction (XRD) patterns of carbon nanotubes. XRD, a rapid analysis technique, is utilized for material identification, notable for its capacity to evaluate both local and overall material characteristics, encompassing lattice structure with phase morphology [15], interlayer distances, among others.

The X-ray diffraction (XRD) analysis was conducted using the XRD-6100 Shimadzu X-ray diffractometer, employing Cu-Kα radiation with a wavelength (λ) of 1.541874 Å. The angular range of 2θ spanned from 5° to 80°, with a step size of 0.05°.

It is well-established that the intensity of diffraction peaks in carbon nanotubes (CNTs) is contingent upon the morphological orientation of the nanotubes. Specifically, when X-rays interact with a single wall of the CNT, they generate peaks (002) along with some parallel (h k l) reflections. As the X-rays traverse through the hollow central core of the CNT, supplementary arrays of hexagonal peaks (h k o) are produced.

The CNTs synthesized in our experiment exhibited two characteristic peaks at 2θ = 25.5° and 43.3°, corresponding to the diffraction from the C(002) and C(100) planes of carbon nanotubes, respectively [16]. Furthermore, literature [17] suggests that in addition to C(100) and C(002), peaks such as C(004) and C(110) may be observable at 2θ = 54.8° and 79.2°. In Figure 3, it is evident that the CNTs possess four characteristic peaks at 2θ = 25.8°, 43.3°, 58.4°, and 78.1°, attributable to the diffraction from the planes C(100), C(002), C(013), and C(016) of the synthesized carbon nanotubes.

Moreover, the XRD pattern suggests the formation of hybrid CNTs in our case. This inference is supported by the most intense diffraction peak observed at 2θ = 24.31, corresponding to the (002) reflection, indicative of a crystalline and cylindrical structure [18]. Additionally, traces of nickel oxide are discernible only in two peaks, specifically at angles 37.9° and 71.8°, with low intensity.

CONCLUSIONS

Utilizing the chemical vapor deposition (CVD) technique at relatively moderate temperatures, employing ethanol vapor as the precursor and hydrogen-reduced nickel oxide nanoparticles as catalysts, a successful synthesis of carbon nanotubes (CNTs) was achieved under controlled environmental conditions. Scanning electron microscopy (SEM)

analysis revealed the formation of fibrous carbon structures, suggestive of hybrid CNTs, indicative of a complex and intertwined nanotube network. Elemental analysis via energy-dispersive X-ray (EDX) spectroscopy exhibited a substantial carbon content, constituting 88% by mass and 94% by atomic number, affirming the predominantly carbonaceous nature of the synthesized material. Furthermore, X-ray diffraction (XRD) investigations demonstrated the presence of four discernible peaks characteristic of carbon nanotubes, emanating from diffraction events associated with the lattice planes C(100), C(002), C(013), and C(016).

The amalgamated findings from these analytical methodologies collectively underscore the successful production of single-walled carbon nanotubes (SWCNTs) under controlled and mild temperature conditions, not surpassing 500°C. This synthesis approach, facilitated by the judicious selection of precursor and catalyst materials, underscores the feasibility of achieving high-quality SWCNTs while mitigating the energy demands associated with traditional high-temperature synthesis methods. The observed structural, elemental, and crystalline characteristics align closely with the anticipated attributes of SWCNTs, further corroborating the efficacy of the employed synthesis strategy. These findings not only contribute to advancing our understanding of CNT synthesis methodologies but also hold promise for various applications in nanotechnology, materials science, and beyond.

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НИЗЬКОТЕМПЕРАТУРНЕ ВИРОЩУВАННЯ ВУГЛЕЦЕВИХ НАНОТРУБОК З ВИКОРИСТАННЯМ НІКЕЛЕВОГО КАТАЛІЗАТОРА

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Це дослідження представляє результати всебічного дослідження виготовлення одностінних вуглецевих нанотрубок (SWCNT) із застосуванням техніки хімічного осадження з парової фази (CVD), причому наночастинки нікелю виступають в якості ключових каталізаторів. Ці наночастинки синтезуються шляхом відновлення прекурсорів оксидів за допомогою водню та стратегічно об'єднуються з парами етанолу як основним джерелом вуглецю. Ефективність і відтворюваність цього методу синтезу ретельно перевірені за допомогою передових аналітичних методів. Особливо слід відзначити продемонстровану здатність проводити процес при відносно низьких температурах, не вище 500°C, що має важливе значення. Такий точний контроль над умовами синтезу не тільки сприяє масштабованості виробництва SWCNT, але також має суттєві наслідки для вдосконалення методологій синтезу наноматеріалів.

Ключові слова: *каталізатори; одностінні вуглецеві нанотрубки; багатошарові вуглецеві нанотрубки; рентгенофазовий аналіз; спектроскопія розсіювання світла; скануюча електронна мікроскопія*