

ARTICLE

A Marker-Based Approach to Investigate the Growth Dynamics of Carbon Nanotube Arrays

Manfred Wuttig^{1,*}

¹ University of Maryland

Abstract

A novel and efficient growth marker technique was developed to facilitate the marking and tracking of the growth dynamics of carbon nanotube (CNT) arrays. This method introduces distinct markers that are clearly visible using scanning electron microscopy (SEM) or optical microscopy, enabling precise and continuous monitoring of the CNT growth process. These markers provide a reliable way to observe growth stages and quantify the growth rate under various experimental conditions, offering valuable insights into the kinetics of CNT formation. By employing this marker technique, we measured the growth rates of CNT arrays across a range of temperatures and acetylene partial pressures, allowing for a comprehensive investigation of the environmental factors influencing CNT synthesis. Detailed analysis of these measurements enabled the calculation of key kinetic parameters, including the activation energy and reaction order of the growth process. These calculations shed light on the underlying mechanisms, revealing critical information about how CNTs develop under different conditions. The experimental data indicate that the growth process is not diffusion-limited. Instead, the calculated activation energy points to the heterogeneous decomposition of acetylene on catalyst particles as the primary rate-determining step. This finding

offers an important contribution to understanding the catalytic interactions that drive CNT growth, helping to refine theoretical models of the process.

Keywords: Carbon Nanotube Arrays, electron microscopy, optical microscopy, heterogeneous decomposition, technological developments

Citation

Manfred Wuttig (2021). A Marker-Based Approach to Investigate the Growth Dynamics of Carbon Nanotube Arrays . Mari Papel Y Corrugado, 2021(1), 1–6.

© The authors. <https://creativecommons.org/licenses/by/4.0/>.

1 Introduction

Since their initial discovery, carbon nanotubes (CNTs) have captivated the attention of researchers in nanoscience and nanotechnology due to their distinctive one-dimensional structure, remarkable mechanical strength, superior electrical properties, and a broad array of potential applications. However, the challenge of synthesizing CNTs with well-defined diameters, lengths, and chiralities remains significant [1]. This challenge is fundamentally linked to our incomplete comprehension of the growth mechanisms that govern CNT formation, making the study of growth kinetics critical to advancing controlled synthesis [2].

Among the various techniques used for CNT production, chemical vapor deposition (CVD) stands out as a prominent method, resulting in three major forms: entangled CNTs produced from catalyst particles, isolated CNTs on substrates, and vertically aligned CNT arrays [3, 4]. While entangled CNTs allow for large-scale production and isolated CNTs offer ease of integration into devices, CNT arrays present a distinct advantage due to their highly ordered configuration, where individual nanotubes are nearly parallel. This consistent orientation

Submitted: 2 November 2020

Accepted: 30 March 2021

Published: 30 June 2021

Vol. 2021, No. 1, 2021.

*Corresponding author:

✉ Manfred Wuttig

wuttig@umd.edu

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

facilitates the measurement of growth rates, as the length of the CNTs is directly proportional to the height of the array [5].

Although, in principle, the growth rate can be calculated by dividing the height of the CNT array by the total growth duration, various experimental factors complicate this approach. In many cases, the height of the array stops increasing even when the reaction time is extended, indicating that the growth process has terminated at an unknown point. Additionally, the growth of CNTs may involve a latency period, making it difficult to pinpoint the exact initiation time of growth [6].

To address these issues, recent research has focused on real-time monitoring of CNT array growth to gain deeper insights into the kinetics. In this paper, we introduce a straightforward growth marker technique that allows for the placement of distinct markers at specific times during the growth of CNT arrays. These markers, visible through both scanning electron microscopy (SEM) and optical microscopy, enable precise tracking of growth rates under varying experimental conditions [7]. By analyzing the growth rates at different temperatures and acetylene partial pressures, we determined the activation energy and reaction order, providing valuable information about the underlying CNT growth mechanisms. This method not only enhances our understanding of CNT growth dynamics but also offers a practical tool for optimizing synthesis processes.

2 Experimental Methodology

Carbon nanotube (CNT) arrays were synthesized using acetylene as the carbon source and silicon wafers with a thin oxide layer (approximately 400–800 nm thick) as substrates. The substrates were coated with a 3–5 nm thick layer of iron, deposited via sputtering, to serve as the catalyst for CNT growth. The growth process was conducted in a horizontal tube furnace, with reaction temperatures ranging from 873 K to 1000 K. The furnace was equipped with a 1-inch diameter quartz tube, which contained the silicon substrate during the reaction.

To explore methods for creating CNT arrays with a specific structure, acetylene gas was intermittently halted for brief periods during growth. Remarkably, this interruption resulted in a distinct linear mark visible in the scanning electron microscope (SEM) images of the CNT arrays, suggesting that this method could be used as a reliable marker for tracking growth.

By carefully recording the time intervals between consecutive gas interruptions, the growth rate could be calculated by measuring the distance between the corresponding line marks on the CNT array.

However, in the tube furnace setup, the feeding gas had to travel a considerable distance from the inlet to the reaction zone, potentially introducing an error in the recorded growth time based on switching events. To minimize this issue and improve the accuracy of the growth marks, we designed a modified quartz boat. This boat featured a single open side facing the gas inlet, allowing for more precise control over the gas flow during the reaction. The silicon substrate (typically 1 cm × 1 cm) was placed on a silica pad and inserted into the cavity of the quartz boat. During growth, an additional stream of argon gas was intermittently introduced for 10–30 seconds to blow away the reaction gas, resulting in a distinct mark on the CNT array.

Repeating this process created a series of line marks, effectively segmenting the CNT array. By measuring the length of each segment, the growth rate over each time interval was determined. This method allowed us to track the growth of the CNT arrays with high precision, facilitating the study of growth kinetics. To further refine the results and understand the temporal variations in growth rate, we analyzed both the first and last segments of the CNT arrays.

To ensure reliable measurement of the growth rates over time, we carefully examined the sequence in which segments formed during the growth process. By analyzing the position of the first and last grown segments, we were able to correlate the timing of the gas interruptions with the actual growth dynamics. The precise timing of each gas interruption was critical for determining the growth rate, as any delay in the gas flow reaching the reaction zone could affect the accuracy of the growth markers.

Additionally, the distance between the growth marks was measured using SEM imaging to determine the length of each segment. These measurements allowed us to calculate the growth rate of CNT arrays at different time intervals. By repeating the gas flow interruption process and marking the array multiple times during a single growth experiment, we created a series of marked segments, enabling us to monitor how the growth rate varied over time.

To investigate the effects of varying experimental conditions on the growth kinetics, we performed

the growth process at different temperatures and acetylene partial pressures. These parameters were systematically varied, and the corresponding growth rates were measured for each set of conditions. This approach allowed us to calculate the activation energy of the growth process and determine the reaction order.

All experiments were conducted in a controlled environment to minimize external factors that could impact growth rates, such as fluctuations in temperature or gas flow. The use of a modified quartz boat ensured that the reaction gases reached the substrate with minimal delay, improving the precision of the growth marks and enhancing the overall accuracy of the growth rate measurements.

By employing this growth marker technique, we were able to gain valuable insights into the kinetics of CNT growth, including the identification of potential rate-limiting steps and the role of the catalyst in the acetylene decomposition process. These findings contribute to a deeper understanding of the growth mechanisms of CNT arrays and provide a foundation for optimizing synthesis processes in the future.

3 Results and Discussion

3.1 Experimental Results

In our growth rate study, carbon nanotube (CNT) arrays were synthesized and marked every five minutes for a total growth period of one hour. Ideally, if growth continued uninterrupted, the resulting CNT array would consist of 12 distinct segments separated by 11 growth markers. However, most CNT arrays ceased growing before the full hour elapsed. For example, as shown in Figure (a), one array formed eight segments, indicating that its growth halted between the seventh and eighth markers. In our experiments, the longest-lasting CNT arrays, grown at temperatures of 913 K and 923 K, contained 10 segments.

At a specific temperature, the growth rate was determined by measuring the length of each segment between successive markers, omitting the first and last segments due to uncertainties regarding the precise start and end of growth. The growth rates were calculated by dividing the length of a given segment by the time interval between two markers. Figure (b) illustrates the measured growth rates across different temperatures, ranging from 873 K to 953 K. At lower temperatures, the growth rate remained relatively constant over time, while at higher temperatures,

the growth rate initially increased before stabilizing, indicating a "steady-state growth" phase. At lower temperatures, this speed-up phase occurred within the first five minutes, whereas at higher temperatures, it extended to 10–15 minutes.

The activation energy, a key parameter for understanding the rate-limiting step of any chemical process, was calculated by averaging the steady-state growth rates at different temperatures. The natural logarithms of the growth rates were plotted against the inverse of the temperature ($1/T$), as shown in Fig. From this Arrhenius plot, the slope of the fitted line yielded an activation energy of 159 ± 5 kJ/mol for our experiments. This value is crucial for understanding the CNT growth mechanism as it directly influences the rate at which reactions occur at various temperatures.

Additionally, to determine the reaction order, the axial growth rate was measured as a function of acetylene partial pressure at 953 K, as shown in Fig. As the acetylene pressure increased, the axial growth rate also increased, suggesting that the reaction is not zero-order. The linearity of the relationship implies a first-order reaction, where the growth rate is directly proportional to the concentration of acetylene in the gas phase.

3.2 Discussion

CNT growth through chemical vapor deposition (CVD) generally involves four key steps: (1) surface reaction at the gas-catalyst interface, (2) diffusion of carbon species through the catalyst particle, (3) precipitation at the catalyst-CNT interface, and (4) CNT formation. These steps are illustrated in Figure 2. The activation energy measured in our experiments aligns with similar studies of carbon atom diffusion in cementite, which report an activation energy of 136 kJ/mol. However, high-resolution transmission electron microscopy (HRTEM) revealed that, during growth, the iron catalyst transitioned to cementite (Fe_3C), consistent with the findings of Schaper and colleagues. Therefore, the catalyst in our experiments cannot be β -iron [8].

Given that our measured activation energy is higher than what is typically associated with carbon diffusion in cementite, we considered two possible explanations. First, if the catalyst behaves in a liquid-like state during CNT growth, as suggested by Kukovitsky and later confirmed by in situ growth monitoring, the diffusion activation energy for such quasi-melts

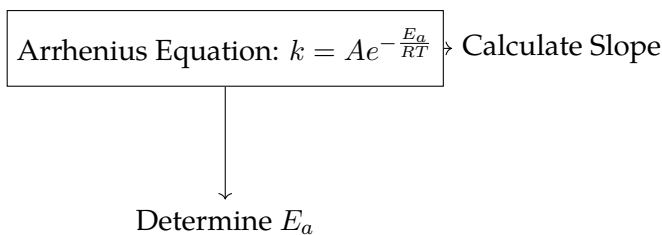
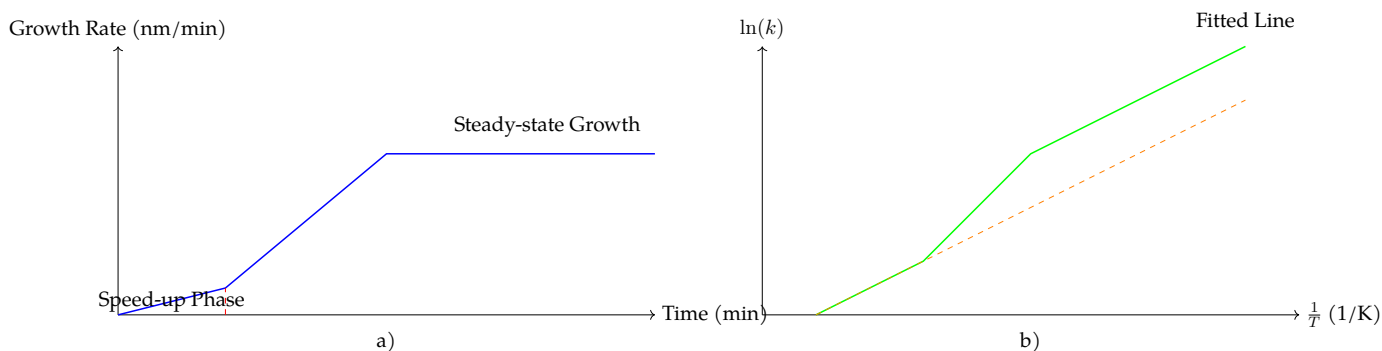


Figure: Activation Energy Determination via Arrhenius Equation



is generally much lower (10 kJ/mol), which is significantly smaller than our measured value of 159 kJ/mol [9]. Additionally, extrapolating previous data on the diffusion of carbon in molten Fe₃C at high pressure yields an activation energy of 37 kJ/mol, still too low to explain our results.

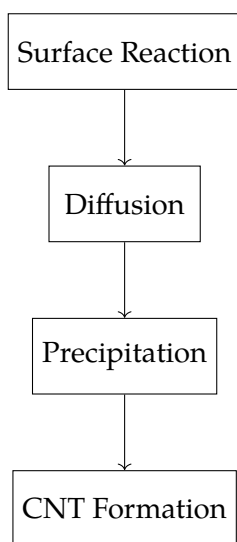


Figure: Four Steps in CNT Growth Process

Alternatively, if the catalyst remains in a solid state, the activation energy could be influenced by the carbon concentration in the catalyst [10]. According to Smoluchowski’s model, higher carbon concentrations in β -iron reduce the activation energy, and an extrapolation of this model suggests an activation energy of about 94 kJ/mol for 25% carbon concentration [11]. However, this is still substantially lower than the 159 kJ/mol we measured, indicating that carbon diffusion within the catalyst is unlikely to be the rate-limiting step.

Our experimental findings also show that the growth rate is strongly dependent on acetylene partial pressure, suggesting that CNT growth is not diffusion-limited. At present, we propose that the surface reaction at the gas-catalyst interface could be responsible for the observed activation energy [12]. Studies by Silcocks on the heterogeneous decomposition of acetylene in the 625–745 K range reported a first-order reaction with an activation energy of 179 kJ/mol. Similarly, Palmer and Dormish observed first-order acetylene decomposition with an activation energy of 109 kJ/mol in the 1333–1528 K range. Thus, it is reasonable to attribute the activation

energy of 159 kJ/mol in our experiments to a surface reaction at the gas-catalyst interface in the 873–1000 K range [13].

Our results do not contradict the diffusion-limited model proposed by [14] for carbon filament growth, which reports a much lower activation energy and growth rate (50 nm/s) with growth terminating within one minute. The differences in growth rate and duration observed in our study—where growth rates are nearly 10 times faster and can last over 30 minutes—may be due to the different morphologies of carbon filaments. Specifically, our experiments produced multi-walled carbon nanotubes (MWCNTs), which exhibit faster growth rates compared to the structures studied by Baker [14–16].

In summary, the CNT growth observed in our experiments is most likely driven by a surface reaction at the gas-catalyst interface rather than carbon diffusion through the catalyst. This insight contributes to a deeper understanding of the kinetics and mechanisms involved in CNT synthesis, laying the groundwork for future optimization of growth conditions.

4 Conclusion

This study has provided new insights into the growth kinetics of carbon nanotube (CNT) arrays synthesized via the chemical vapor deposition (CVD) method. By employing a novel growth marking technique, we successfully measured growth rates under varying conditions of temperature and acetylene partial pressure, enabling us to gain a deeper understanding of the CNT growth process and its underlying mechanisms.

Our results demonstrated that the CNT growth rate varies significantly with temperature. At lower temperatures (below 913 K), the growth rates remained relatively constant, while at higher temperatures (above 913 K), an initial acceleration phase was observed before the growth stabilized into a steady-state. This indicates that CNT growth does not follow a purely diffusion-limited model, as previously proposed for other carbon filaments. Instead, our findings suggest a more complex interaction between surface reactions and diffusion processes at different temperature ranges.

The determination of the activation energy ($E_a = 159 \pm 5$ kJ/mol) provided further evidence that the growth mechanism in our experiments is not limited by carbon diffusion through the catalyst particle. Previous

studies have shown that carbon atom diffusion in β -iron or cementite catalysts typically exhibits lower activation energies, suggesting that the primary rate-limiting step in our system is likely a surface reaction occurring at the gas-catalyst interface. The first-order reaction kinetics with respect to acetylene partial pressure further support this hypothesis, as the growth rate was strongly dependent on the concentration of acetylene in the system.

Comparative analysis with prior studies indicates that the differences in growth rates and activation energies between our experiments and those conducted by Baker and colleagues may be attributed to the differing morphologies of carbon filaments. While their model assumed diffusion-limited growth for carbon filaments, our multi-walled carbon nanotubes (MWCNTs) grew at rates nearly ten times faster and continued to grow for over 30 minutes, suggesting that the growth process in our case was dominated by surface reactions rather than diffusion constraints.

Moreover, the segmented growth patterns observed in our CNT arrays, induced by interruptions in acetylene gas flow, allowed us to accurately measure growth rates and investigate the temporal evolution of CNT growth. This method proved effective for tracking CNT growth kinetics in situ and provided valuable data for determining the steady-state growth phase and the time required to reach it.

Overall, our study challenges the traditional diffusion-limited model for CNT growth and emphasizes the role of surface reactions at the gas-catalyst interface as a key factor in controlling growth rates. The measured activation energy and reaction order align with previous studies on acetylene decomposition, suggesting that similar processes may govern CNT growth in our experimental conditions. Future work could focus on refining the understanding of these surface reactions and further optimizing growth conditions to enhance control over CNT properties such as length, diameter, and chirality.

In conclusion, this study contributes to the growing body of knowledge on CNT growth mechanisms and provides a framework for future research aimed at optimizing CNT synthesis for various nanotechnology applications. By elucidating the kinetic factors governing CNT growth, we pave the way for more precise control over the production of high-quality CNT arrays, which have vast potential in fields ranging from electronics to materials science.

References

- [1] Duan, Lian, and Levent Yobas. "Label-free multiplexed electrical detection of cancer markers on a microchip featuring an integrated fluidic diode nanopore array." *ACS nano* 12.8 (2018): 7892-7900.
- [2] Forouzanfar, Shahrzad. "Investigation of Carbon-based Label-Free Electrochemical Aptasensors for Point-of-Care Cancer Biomarker Detection." (2021).
- [3] Barani, Mahmood, et al. "Nanotechnology in ovarian cancer: Diagnosis and treatment." *Life Sciences* 266 (2021): 118914.
- [4] Teles, F. R. R., and L. P. Fonseca. "Trends in DNA biosensors." *Talanta* 77.2 (2008): 606-623.
- [5] Bajaj, Avinash, et al. "Detection and differentiation of normal, cancerous, and metastatic cells using nanoparticle-polymer sensor arrays." *Proceedings of the National Academy of Sciences* 106.27 (2009): 10912-10916.
- [6] Nawaz, Muhammad Azhar Hayat, et al. "One step assembly of thin films of carbon nanotubes on screen printed interface for electrochemical aptasensing of breast cancer biomarker." *Sensors* 16.10 (2016): 1651.
- [7] Piro, Benoît, and Steeve Reisberg. "Recent advances in electrochemical immunosensors." *Sensors* 17.4 (2017): 794.
- [8] Wang, Di, Fei Dai, and Xiaopeng Ning. "Risk assessment of work-related musculoskeletal disorders in construction: State-of-the-art review." *Journal of Construction Engineering and management* 141.6 (2015): 04015008.
- [9] Cheng, Dan, et al. "One-step facile synthesis of hyaluronic acid functionalized fluorescent gold nanoprobe sensitive to hyaluronidase in urine specimen from bladder cancer patients." *Talanta* 130 (2014): 408-414.
- [10] Zhu, Jie, et al. "Protein assembly by design." *Chemical reviews* 121.22 (2021): 13701-13796.
- [11] Sahu, Sujit Kumar, et al. "Shape reconstruction processes for interventional application devices: State of the art, progress, and future directions." *Frontiers in Robotics and AI* 8 (2021): 758411.
- [12] Campuzano, Susana, Paloma Yáñez-Sedeño, and José M. Pingarrón. "Diagnostics strategies with electrochemical affinity biosensors using carbon nanomaterials as electrode modifiers." *Diagnostics* 7.1 (2016): 2.
- [13] Jo, Myung Hyun, W. Taylor Cottle, and Taekjip Ha. "Real-time measurement of molecular tension during cell adhesion and migration using multiplexed differential analysis of tension gauge tethers." *ACS Biomaterials Science & Engineering* 5.8 (2018): 3856-3863.
- [14] Fottner, Johannes, et al. "Autonomous systems in intralogistics: state of the Art and future research challenges." *Logistics Research* 14.1 (2021): 1-41.
- [15] Xu, Sai, et al. "based upconversion fluorescence resonance energy transfer biosensor for sensitive detection of multiple cancer biomarkers." *Scientific Reports* 6.1 (2016): 23406.
- [16] Chen, Chunpeng James, et al. "Role of the genomics–phenomics–agronomy paradigm in plant breeding." *Plant Breeding Reviews* 46 (2022): 627-673.