Erzincan Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
2022 15(1), 296-303
ISSN: 1307-9085, e-ISSN: 2149-4584
Araştırma Makalesi

Erzincan University
Journal of Science and Technology
2022, 15(1), 296-303
DOI: 10.18185/erzifbed.1036126
Research Article

Large-area synthesis of vertically aligned carbon nanotubes growth on the aluminum foil via FCCVD method

Yaşar Özkan YEŞİLBAĞ[1]*, Fatma Nur TUZLUCA YEŞİLBAĞ[1], Ahmad HUSEYİN[2], Ahmad Jalel Salih SALİH[2], Eda Nur DEMİREZ[3]

[1]Erzincan Binali Yıldırım University, Department of Physics Erzincan 24100, Turkey
[2]Erzincan Binali Yıldırım University Graduate School of Natural and Applied Sciences, Department of Pyhsics, Erzincan 24100 , Turkey
[3]Erzincan Binali Yıldırım University Graduate School of Natural and Applied Sciences, Department of Nanoscience and Nanoengineering, Erzincan 24100, Turkey

Geliş / Received: 14/12/2021, Kabul / Accepted: 10/03/2022

Abstract

In this study, VA-CNTs were synthesized homogeneously on Al foil at 610 °C temperature by Floating Catalyst Chemical Vapor Deposition (FCCVD) method in a tube furnace. While ethanol was used as the carbon source, ferrocene was used as the catalyst. VA-CNTs with diameters in the range of ~10-15 nm and lengths in the range of ~30-35 µm were obtained. Structural and morphological analyzes of VA-CNTs were determined using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersion X-Ray Spectroscopy (EDS), Raman Spectroscopy and X-Ray Photoelectron Spectroscopy (XPS). These VA-CNTs, synthesized by the FCCVD method on an Al foil in a large area, have the potential applications to be used especially in energy storage, optoelectronic, and sensor.

Keywords: VA-CNTs, FCCVD, aluminum foil

FCCVD yöntemi ile alüminyum folyo üzerinde dikey olarak hizalanmış karbon nanotüp büyümesinin geniş alan sentezi.

Öz

Bu çalışmada, yatay bir tüp fırında FCCVD yöntemiyle 610 °C sıcaklıkta Al folyo üzerine VA-CNT’ler homojen bir şekilde sentezlenmiştir. Karbon kaynağı olarak etanol kullanılırken katalizör olarak da ferrosen kullanılmıştır. Çapları ~10-15 nm aralığında, uzunlukları ise ~30-35 µm aralığında değişen VA-CNT'ler elde edilmiştir. VA-CNT'lerin yapısal ve morfolojik analizleri, X-Işını Kırınım (XRD), Alan Emisyon Taramalı Elektron Mikroskobu (FESEM), Enerji Dağılım X-Işını Spektroskopisi (EDS), Raman Spektroskopisi ve X-Işını Fotoelektron Spektroskopisi (XPS) kullanılarak belirlenmiştir. Geniş bir alanda Al folyo üzerinde FCCVD yöntemiyle sentezlenen bu VA-CNT'ler, özellikle enerji depolama, optoelektronik ve sensör uygulamalarında kullanılabilme potansiyeline sahiptir.

Anahtar Kelimeler: VA-CNTs, FCCVD, alüminyum folyo

*Corresponding Author: oyesilbag@erzincan.edu.tr

1. Introduction

Carbon nanotubes (CNTs) are one-dimensional (1D) nanomaterials with a unique structure, varying in length in micrometers and diameters in nanometers. CNTs are formed by wrapping one or more layers of graphite and have sp^2 bonding in a cylindrical hexagonal network structure. (Rafique et al., 2016; Shi and Plata 2018). CNTs are classified as single-walled (SWCNT), double-walled (DWCNT), or multi-walled (MWCNT) (Rafique et al., 2016). Besides its light weight and high specific surface area, CNTs have superior mechanical, thermal, chemical, and electrical properties, thus attracting attention for many applications in many fields (Yilmaz et al., 2017; Yesilbag et al., 2021). CNTs most important applications are in electronics, optoelectronics, and energy storage applications such as solar cells, sensors, transistors, and batteries, field emission characteristics (Bondavalli et al., 2009; Chachuli et al., 2021; Jo et al., 2003; Jeon et al., 2019; Wang et al., 2003).

There are three main methods for synthesizing CNTs using arc discharge, laser ablation and chemical vapor deposition (CVD) (Manawi et al., 2018). The CVD method is the most widely used among these methods (Chen et al., 2014). CVD system is further divided into two types, the first is substrate-based CVD, in which the catalyst is deposited on the support layer previously deposited on the substrate (Yaglioglu et al., 2012), the second is called the Floating Catalyst CVD (FCCVD), where the catalyst is injected into the gas phase with the carbon source to the system (Chen et al., 2019). This FCCVD method is suitable for continuous production of CNTs and contributes to the reduction of costs (Ionescu et al., 2011). FCCVD method can also be used by dividing it into two stages, in which the catalyst is preheated and then transferred to the reaction area by the carrier gas, and hydrocarbon gas is released in the second stage (Kinoshita et al., 2019). CNTs can be grown on a variety of substrates such as silicon, quartz, aluminum, stainless steel, and copper (Yilmaz et al., 2017). Aluminum (Al) is the most widely used substrate due to its low bulk density, good electrical conductivity, and high flexibility. Direct growth of VA-CNTs (Vertical Aligned Carbon Nanotubes) in CVD system on Al foil is limited by the melting point of Aluminum (640 to 660°C). Synthesis of VA-CNTs on Al foil at a competitive growth rate paves the way for its industrial progress. These new progresses are the result of careful control of the tuning parameters, especially the Fe/C ratio in the source flow. Lowering the growth temperature allows the formation of many small iron-based nanoparticles, so that the VA-CNT forest has a density of about (1011 CNT/cm^2) at 615 °C with an outer diameter of CNT of about 10 nm and a narrow distribution (Nassoy et al., 2019).

2. Materials and Methods

VA-CNTs on Al foil (15x10 cm) were synthesized by the FCCVD method in a horizontal tube furnace shown in Figure 1a. Since it is important to prevent aggregation of Fe catalyst nanodroplet on the substrate, the natural Al_2O_3 layer on the Al foil surface provides this aggregation (Raji et al., 2017). In the experiment, ethanol (C_2H_5OH) was used as the carbon source and $Fe(C_5H_5)_2$ was used as the catalyst. Argon and hydrogen gases were used in the experiment. Argon was used as carrier gas. While argon is used as a carrier gas, H_2 is used to reduce and remove the amorphous carbon formed in the environment. H_2 plays an important role in CNT growth. Because the H_2 in the environment adjusts the reaction rate and optimizes the activity of catalyst particles and CNT growth (Behr et al., 2010). First, 1% wt of ferrocene was dissolved in 10 ml of ethanol on a magnetic stirrer. Ar (100 sccm) and H_2 (60 sccm) gases were introduced into the system until the temperature reached 610 °C. When the temperature reached 610 °C, the Ar and H_2 gas flow rates were changed to 500 sccm and 300 sccm, respectively, while the source solution was sent to the system with a carrier gas with an injection rate of 10 ml/h using a syringe pump and the growth period was started. After 20 minutes, the solution flow was stopped, and the sample was cooled to room temperature in the presence of Ar and H_2 gases. A photograph of the Al foil on which the VA-CNTs grew after the experiment is given in Figure 1b.

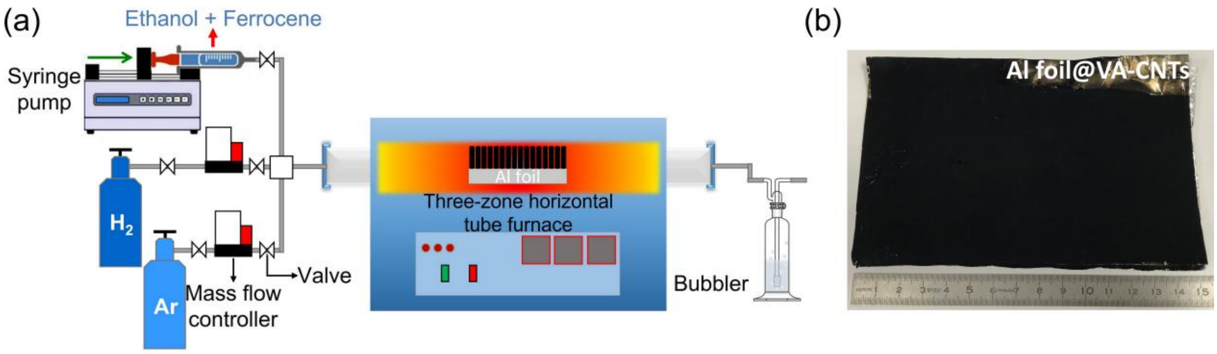

Figure 1. (a) Schematically illustration of the experimental system, **(b)** A picture of the VA-CNTs growing on aluminum foil.

3. Results and Discussion

FESEM (FEI Quanta 450 FEG) images of VA-CNTs grown on the Al foil surface are shown in Figure 2a-d. As seen from the FESEM results, VA-CNTs grew densely and homogeneously on the Al substrate. The diameters of CNTs vary between ~10-15 nm and their lengths vary between ~30-35 µm (Figure 2c). Besides as seen in Figure 2d, VA-CNTs adhere well to the

Al foil surface. In Figure 2e, the EDS analysis taken over the entire surface, the atomic concentrations of C, O, Al, and Fe elements in the structure are 89.7, 1.67, 8.42, and 0.15, respectively.

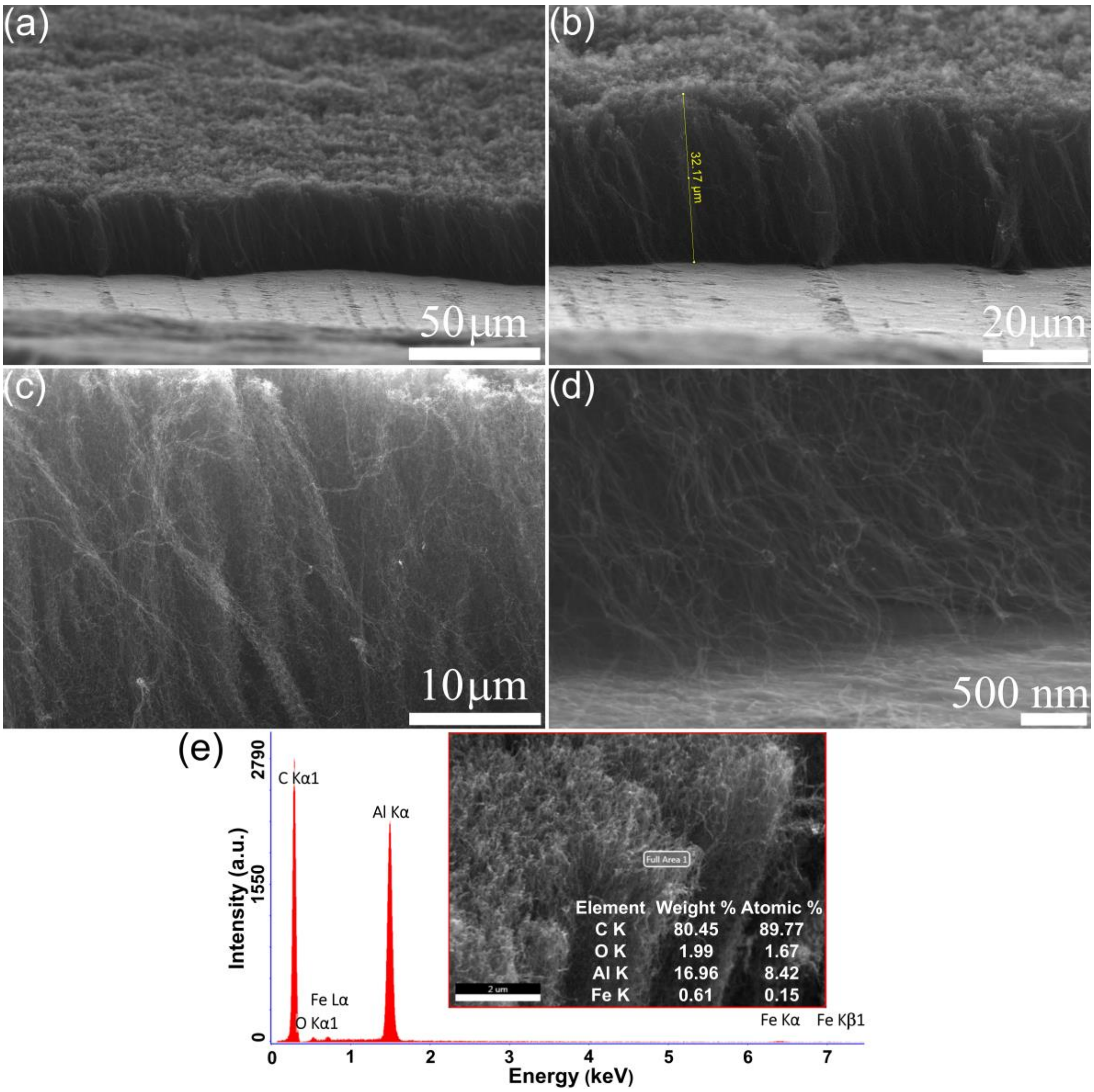

Figure 2. (a-d) FESEM images of VA-CNTs on Al foil and **(e)** EDS analysis.

Figure 3 shows the Raman (WITec alpha300R, λ=532 nm) spectrum of the sample. In the Raman spectrum D, G and 2D bands can be seen around 1335 cm^{-1}, 2574 cm^{-1} and 2665 cm^{-1}, respectively. The D band around 1335 cm^{-1} is generally called the defect band, and the intensity of the G band is generally used as a measure of the quality of CNTs. The I_D/I_G intensity ratio in the Raman spectrum is 1.13. This indicates that there are defects in the structure of CNTs as well as more intense growth of CNTs.

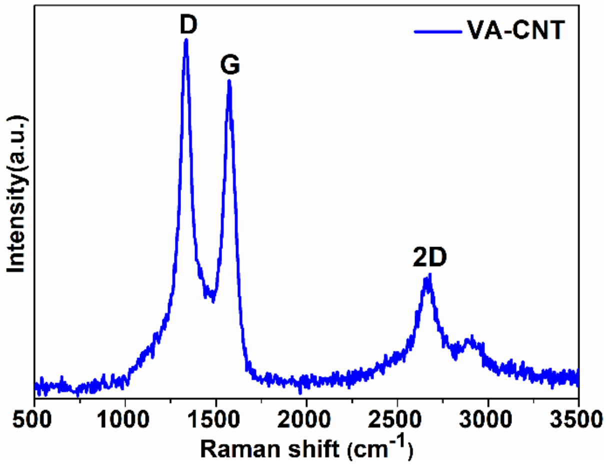

Figure 3. Raman analysis of the VA-CNTs.

The XRD (PANalytical Empyrean, Cu-Kα, λ=1.54060 Å) pattern of the VA-CNT structure taken in the range of 10^o-80^o (2θ) is given in Figure 4. According to JCPDS Card No: 26-1079, the XRD peak in 26.6 of VA-CNTs corresponds to the (002) plane of graphitic carbon at high temperature. The good intensity of this peak indicates that VA-CNTs have a good crystalline structure.

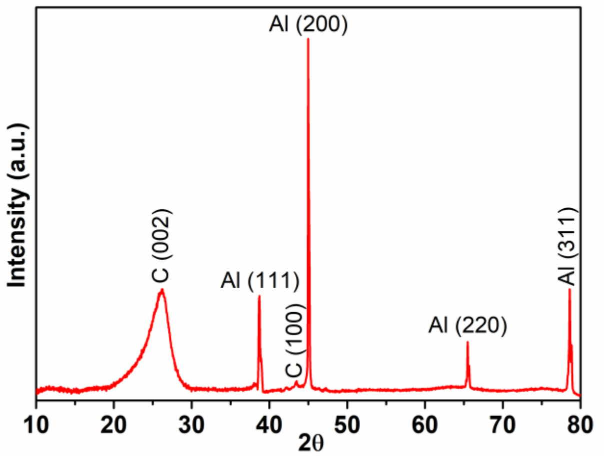

Figure 4. XRD analysis of the VA-CNTs.

XPS (SPECS-Flex, Al-K_{α}) analysis of VA-CNTs is given in Figure 5. As seen in Figure 5, there are C and O elements in the full spectrum. The high-resolution C 1s peak in Figure 5b has four peaks at 284.5 eV, 285.4 287.8 eV and 290.6 eV, corresponding to C-C, C=C, C=O and O=C-OH binding energies, respectively (Jerng et al., 2011; Yesilbag et al., 2021). In addition, the O 1s peak is also due to oxygen adsorbed on the carbon surface (Figure 5c).

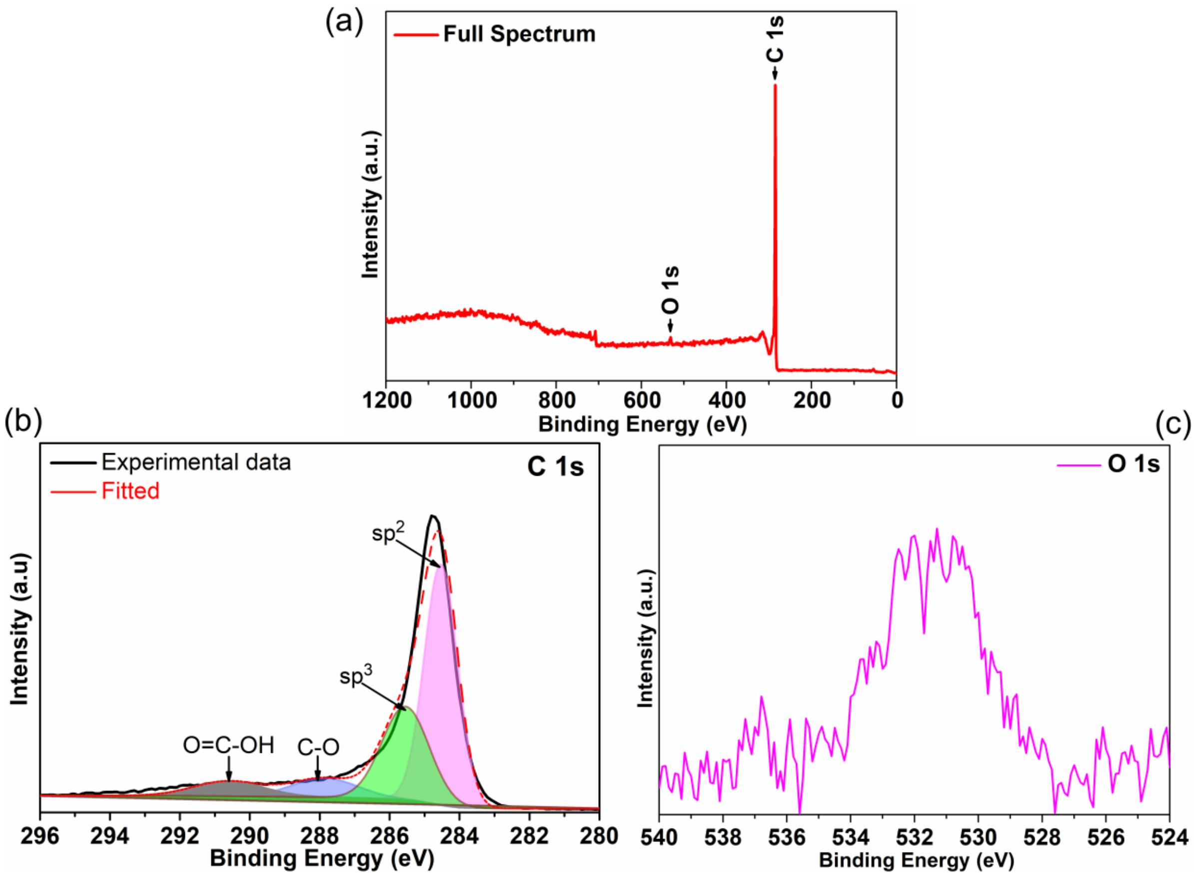

Figure 5. **(a)** Full spectrum XPS analysis **(b)** C1s, **(c)** O1s high resolution XPS spectra of VA-CNTs.

4. Conclusion

VA-CNTs were grown on Al foil in a tube furnace. Ethanol and ferrocene were used as carbon source and catalyst, respectively. VA-CNTs with diameters in the range of ~10-15 nm and lengths in the range of ~30-35 μm were obtained. The fact that it is inexpensive, flexible, readily available, and has a natural oxide layer has made Al foil a good substrate material for the growth of CNTs. In addition, VA-CNTs grown by this method can be used in applications with large surface areas.

Acknowledgements

This study was supported by the TUBITAK under Grant Number: 217M323.

Author Contributions

Yasar Ozkan Yesilbag: Ideas; formulation or evolution of overarching research goals and aims, Acquisition of the financial support for the project leading to this publication.

Fatma Nur Tuzluca Yesilbag: Ideas; formulation or evolution of overarching research goals and aims, preparation, creation and/or presentation of the published work, specifically visualization/ data presentation.

Ahmad Huseyin: Conducting a research and investigation process, specifically performing the experiments, or data/evidence collection.

Ahmad Jalel Salih SALİH: Performing the experiments, or data/evidence collection.

Eda Nur DEMİREZ: Performing the experiments, or data/evidence collection.

Ethics in Publishing
There are no ethical issues regarding the publication of this study.

References
Behr, M. J., Gaulding, E. A., Mkhoyan, K. A., & Aydil, E. S. 2010. "Effect of hydrogen on catalyst nanoparticles in carbon nanotube growth". *Journal of Applied Physics*, 108(5), 053303.

Bondavalli, P., Legagneux, P., & Pribat, D. 2009. "Carbon nanotubes based transistors as gas sensors: State of the art and critical review". *Sensors and Actuators B: Chemical*, 140(1), 304-318.

Chachuli, S. A. M., Hamidon, M. N., Ertugrul, M., Mamat, M. S., Coban, O., Tuzluca, F. N., Yesilbag, Y. O., & Shamsudin, N. H. 2021. "Effects of MWCNTs/Graphene Nanoflakes/MXene addition to TiO_2 thick film on hydrogen gas sensing". *Journal of Alloys and Compounds*, 160671.

Chen, D. R., Chitranshi, M., Schulz, M., & Shanov, V. 2019. "A Review of Three Major Factors Controlling Carbon Nanotubes Synthesis from the Floating Catalyst Chemical Vapor Deposition". *Nano Life*, 9(04), 1930002.

Chen, Y., Zhang, Y., Hu, Y., Kang, L., Zhang, S., Xie, H., ... & Zhang, J. 2014. "State of the art of single- walled carbon nanotube synthesis on surfaces". *Advanced Materials*, 26(34), 5898-5922.

Ionescu, M. I., Zhang, Y., Li, R., Sun, X., Abou-Rachid, H., & Lussier, L. S. 2011. "Hydrogen-free spray pyrolysis chemical vapor deposition method for the carbon nanotube growth: parametric studies". *Applied surface science*, 257(15), 6843-6849.

Jerng, S. K., Yu, D. S., Lee, J. H., Kim, C., Yoon, S., & Chun, S. H. 2011. "Graphitic carbon growth on crystalline and amorphous oxide substrates using molecular beam epitaxy". *Nanoscale research letters*, 6(1), 1-6.

Jo, S. H., Tu, Y., Huang, Z. P., Carnahan, D. L., Wang, D. Z., & Ren, Z. F. 2003. “Effect of length and spacing of vertically aligned carbon nanotubes on field emission properties”. *Applied Physics Letters*, 82(20), 3520-3522.

Kinoshita, T., Karita, M., Nakano, T., & Inoue, Y. 2019. “Two step floating catalyst chemical vapor deposition including in situ fabrication of catalyst nanoparticles and carbon nanotube forest growth with low impurity level”. *Carbon*, 144, 152-160.

Manawi, Y. M., Samara, A., Al-Ansari, T., & Atieh, M. A. 2018. “A review of carbon nanomaterials’ synthesis via the chemical vapor deposition (CVD) method”. *Materials*, 11(5), 822.

Nassoy, F., Pinault, M., Descarpentries, J., Vignal, T., Banet, P., Coulon, P. E., Goislard De Monsabert, T., Hauf, H., Aubert, P-H., Reynaud, C., & Mayne-L’Hermite, M. 2019. “Single-step synthesis of vertically aligned carbon nanotube forest on aluminium foils”. *Nanomaterials*, 9(11), 1590.

Rafique, I., Kausar, A., Anwar, Z., & Muhammad, B. 2016. “Exploration of epoxy resins, hardening systems, and epoxy/carbon nanotube composite designed for high performance materials: A review”. *Polymer-Plastics Technology and Engineering*, 55(3), 312-333.

Raji, A. R. O., Villegas Salvatierra, R., Kim, N. D., Fan, X., Li, Y., Silva, G. A. L., Sha, J., & Tour, J. M. 2017. “Lithium batteries with nearly maximum metal storage”. *ACS nano*, 11(6), 6362-6369.

Shi, W., & Plata, D. L. 2018. “Vertically aligned carbon nanotubes: Production and applications for environmental sustainability”. *Green Chemistry*, 20(23), 5245-5260.

Wang, G. X., Ahn, J. H., Yao, J., Lindsay, M., Liu, H. K., & Dou, S. X. 2003. “Preparation and characterization of carbon nanotubes for energy storage”. *Journal of power sources*, 119, 16-23.

Yaglioglu, O., Cao, A., Hart, A. J., Martens, R., & Slocum, A. H. 2012. “Wide range control of microstructure and mechanical properties of carbon nanotube forests: a comparison between fixed and floating catalyst CVD techniques”. *Advanced Functional Materials*, 22(23), 5028-5037.

Yesilbag, Y. O., Yesilbag, F. N. T., Huseyin, A., Tuzluca, M., Ismail, I., & Ertugrul, M. 2021. “Synthesis and characterization of graphene/carbon nanotube hybrid: effects of Ni catalyst thickness and H_2 flow rate on growth and morphological structure”. *Journal of Materials Science: Materials in Electronics*, 32(6), 7943-7955.

Yilmaz, M., Raina, S., Hsu, S. H., & Kang, W. P. 2017. “Growing micropatterned CNT arrays on aluminum substrates using hot-filament CVD process”. *Materials Letters*, 209, 376-378.