



## Article

# Innovative Variation in the Morphological Characteristics of Carbon Nanowalls Grown on a Molybdenum Disulfide Interlayer

Chulsoo Kim <sup>1</sup>, Kangmin Kim <sup>1</sup>, Seokhun Kwon <sup>1</sup>, Hyunil Kang <sup>1</sup>, Byungyou Hong <sup>2</sup> and Wonseok Choi <sup>1,\*</sup>

<sup>1</sup> Department of Electrical Engineering, Hanbat National University, Daejeon 34158, Republic of Korea

<sup>2</sup> School of Electronic and Electrical Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea

\* Correspondence: wschoi@hanbat.ac.kr

**Abstract:** Carbon is a material with interesting properties which exists in large quantities on Earth, so many studies involving carbon have been conducted. In particular, nano-sized carbon allotropes, referred to as carbon nanomaterials, comprise the subject of various studies currently underway. The electrical, chemical, physical properties of carbon nanowalls (CNWs) are modified by parameters such as surface density, height and thickness. These characteristics have significant effects on CNWs and can be adjusted as a growth interlayer. It was confirmed that the molybdenum disulfide (MoS<sub>2</sub>) interlayer synthesized in this paper by radio frequency (RF) magnetron sputtering altered the morphological characteristics of the CNWs, including its shaped edge, pores diameter and density. We provide interesting results through FE-SEM, EDS and Raman analysis in this paper. Based on the Raman analysis, both the D-peak of carbon and the I<sub>D</sub>/I<sub>G</sub> ratio decreased. Through this study, the effect of MoS<sub>2</sub> on the morphological characteristics of CNWs was confirmed.

**Keywords:** carbon nanowall; molybdenum disulfide; interlayer; morphological characteristics



**Citation:** Kim, C.; Kim, K.; Kwon, S.; Kang, H.; Hong, B.; Choi, W.

Innovative Variation in the Morphological Characteristics of Carbon Nanowalls Grown on a Molybdenum Disulfide Interlayer.

*Nanomaterials* **2022**, *12*, 4334.

<https://doi.org/10.3390/nano12234334>

nano12234334

Academic Editor: Marius Dobromir

Received: 18 November 2022

Accepted: 5 December 2022

Published: 6 December 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Carbon-based materials have the advantages offered by metals, chemicals and ceramics. They have excellent strength and flexibility, are lightweight and have high electrical conductivity. In addition, carbon-based materials are used in various fields around the world because of the chemical stability they offer [1,2]. Various carbon allotropes exist, depending on hybridization bonding, such as sp<sup>2</sup>, sp<sup>3</sup>, corresponding to graphene, graphite, and diamond. Among them, carbon nanowalls (CNWs), or the vertically oriented structures of graphene [3–6], are promising candidates with very large specific surface areas [7]. Among carbon allotropes, CNWs can be grown by plasma enhanced chemical vapor deposition (PECVD) at relatively low temperature [8]. Without catalysts, CNWs can be grown on various substrates, such as glass and polymer-based substrates. In addition, CNWs exhibit various physical properties depending to the morphological characteristics. Variations in morphological characteristics depends on several parameters, such as the reactant gas, power and working pressure [9]. These results can be confirmed through diverse literature reports, but studies on morphological characteristics attributed to the interlayer remain limited [10]. However, our research group did not control parameters such as the ratio of the reaction gas, including the microwave power and the working pressure, and the variation in morphological characteristics of the CNWs is brought on by the MoS<sub>2</sub> interlayer. MoS<sub>2</sub>, one of the representative materials of transition metal dichalcogenides (TMDC), is a two-dimensional material with excellent physicochemical properties [11,12] which has been in the spotlight as a semiconductor material that can replace graphene. Although many studies on carbon-based materials and MoS<sub>2</sub> hybrid composites have been conducted around the world, there are limitations in that the synthesis is difficult and time-consuming [13]. In this paper, a MoS<sub>2</sub> interlayer was synthesized on a glass substrate using an radio frequency (RF) magnetron sputtering system to vary the morphological

characteristics of CNWs, which shortened the synthesis time and obtained high purity MoS<sub>2</sub>. It was characterized through FE-SEM, EDS and Raman analysis. CNWs grown on the MoS<sub>2</sub> interlayer showed interesting morphological characteristics. These results are attributed to the initial growth of CNWs in the MoS<sub>2</sub> crystal plane, and could also be due to van der Waals forces between the surface of MoS<sub>2</sub> and graphene sheets [14].

## 2. Experimental Method

### 2.1. Preparation of Substrate

A glass substrate consisting of amorphous SiO<sub>2</sub> was used. In the substrate cleaning process step, ultrasonic degreasing of the glass substrates was performed for 10 min in the following order: trichloroethylene (TCE), acetone, methanol, and deionized water (DI water).

### 2.2. MoS<sub>2</sub> Interlayer Synthesis and Annealing

The MoS<sub>2</sub> interlayer was synthesized through an RF magnetron sputtering system using a molybdenum disulfide (MoS<sub>2</sub>, 99.99%) 4-inch target (Table 1). Afterwards, it was annealed in a vacuum chamber at 400 °C and 10<sup>−6</sup> Torr for 40 min.

**Table 1.** Sputtering system parameters for MoS<sub>2</sub> interlayer synthesis.

| Parameters       | MoS <sub>2</sub>            |
|------------------|-----------------------------|
| RF Power         | 200 W                       |
| Base Pressure    | 10 <sup>−6</sup> Torr       |
| Working Pressure | 1.5 × 10 <sup>−2</sup> Torr |
| Temperature      | Room Temperature            |
| Synthesis Time   | 10 min                      |

### 2.3. Growth of the Carbon Nanowall

The prepared MoS<sub>2</sub> samples were placed in a PECVD (2.45 GHz microwave) chamber, and a base vacuum at 10<sup>−6</sup> Torr was applied for 24 h. After 40 sccm of hydrogen (H<sub>2</sub>) gas and 20 sccm of methane (CH<sub>4</sub>) gas were injected into the chamber, a plasma was formed using 1300 W of 2.45 GHz microwave power. During the CNW growth process, the temperature and pressure were maintained at 600 °C and 4 × 10<sup>−2</sup> Torr, respectively (Table 2).

**Table 2.** Process parameters of PECVD method for CNW growth.

| Parameters       | CNW                                                |
|------------------|----------------------------------------------------|
| Microwave Power  | 1300 W                                             |
| Reaction Gas     | H <sub>2</sub> 40 sccm and CH <sub>4</sub> 20 sccm |
| Base pressure    | 10 <sup>−6</sup> Torr                              |
| Working Pressure | 4 × 10 <sup>−2</sup> Torr                          |
| Temperature      | 600 °C                                             |
| Growth Time      | 5, 10 and 15 min                                   |

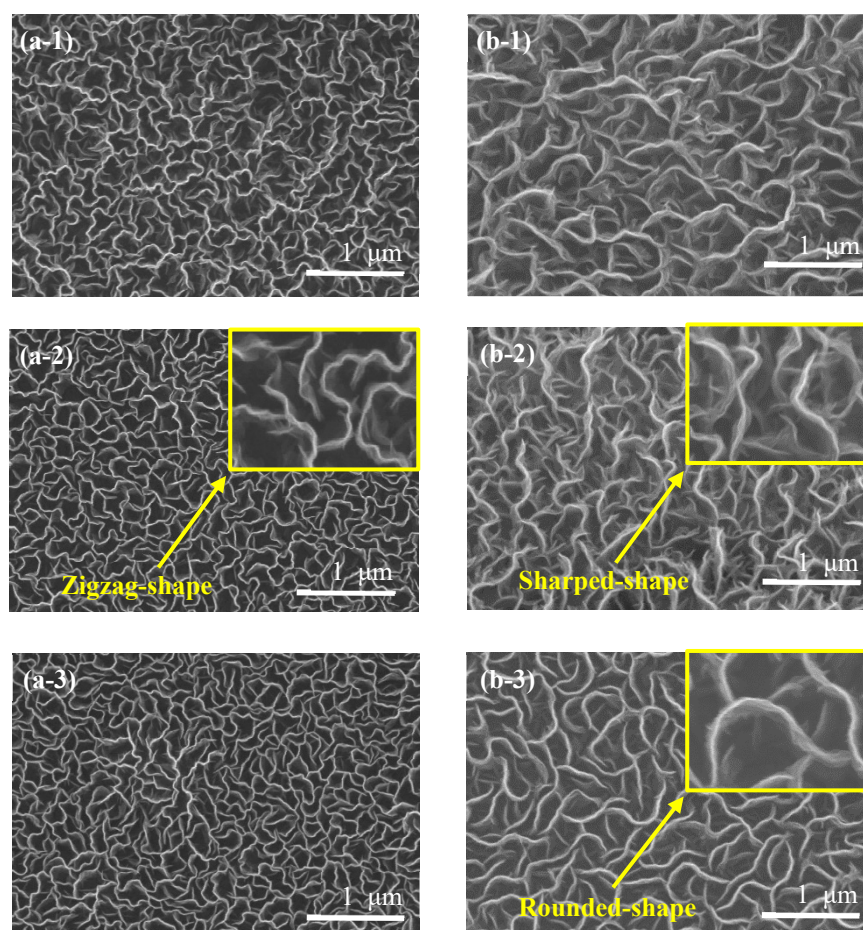
### 2.4. Characterization and Analysis of Materials

In this study, the morphological characteristics of CNWs were analyzed through field-emission scanning electron microscopy (FE-SEM, HITACH, Japan, S-4800) at 15 kV and energy-dispersive X-ray spectroscopy (EDS). In addition, the intrinsic properties of carbon, such as the graphitization degree and defects of CNW were analyzed using Raman spectroscopy (HORIBA, Japan, LabRAM HR-800). The laser power was 3 mW, the excitation wavelength was 532 nm and a ×50 objective with NA = 0.5 was used.

### 3. Results and Discussion

#### 3.1. Morphological Characteristics of Carbon Nanowalls

Figure 1(a-1–a-3) shows the surface FE-SEM image of the CNW grown on a glass substrate. The CNW surface is serpentine and disordered regardless of the growth time. It exhibits morphological characteristics of primitive CNWs and is defined by the zigzag-shaped edge [15], shown in Figure 1(a-2). This is because CNW grows anisotropically or is disordered due to defects in the graphene sheets that occur during the initial growth process [16]. Figure 1(b-1–b-3) shows the surface FE-SEM image of CNW growth on the MoS<sub>2</sub> interlayer. In this case, Figure 1(b-1,b-2) shows sharp-edge shapes [17,18] compared to CNWs grown directly on the glass substrate. As the deposition time was increased to 15 min, a round-edged shape formed in Figure 1(b-3), and compared to Figure 1(a-1–a-3), the density was lower and the pore diameter between the edges increased. The CNW grown on the MoS<sub>2</sub> interlayer for 10 min showed the greatest deformation in surface morphological characteristics of the existing CNW.



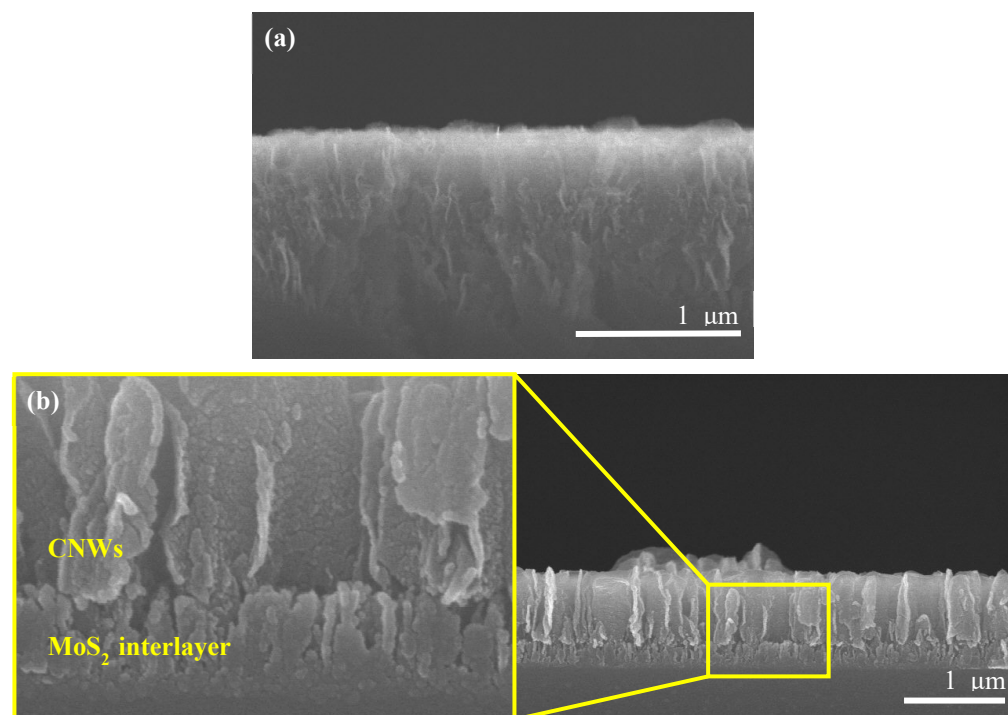
**Figure 1.** FE-SEM surface images of grown CNWs on the glass substrate with a growth time of (a-1) 5 min, (a-2) 10 min and (a-3) 15 min. Samples (b-1–b-3) are FE-SEM surface images of CNWs grown on the MoS<sub>2</sub> interlayer for 5 min, 10 min and 15 min, respectively.

Cross-sectional FE-SEM images of CNW/MoS<sub>2</sub> samples synthesized on glass substrates for 10 min each are shown in Figure 2. The height is 250 nm for MoS<sub>2</sub> and 750 nm for CNWs. The vertically oriented MoS<sub>2</sub> sheet and graphene sheet regions have different diameters and densities. For this reason, we show a clear interface between MoS<sub>2</sub> and the CNW. They grow at a slower rate than native CNWs because of the initial growth process of CNW occurring in macropores (<50 nm) in the MoS<sub>2</sub> interlayer (Figure 3). For a 10 min synthesis, CNW grown directly on a glass substrate grew to a height of about 1 μm,

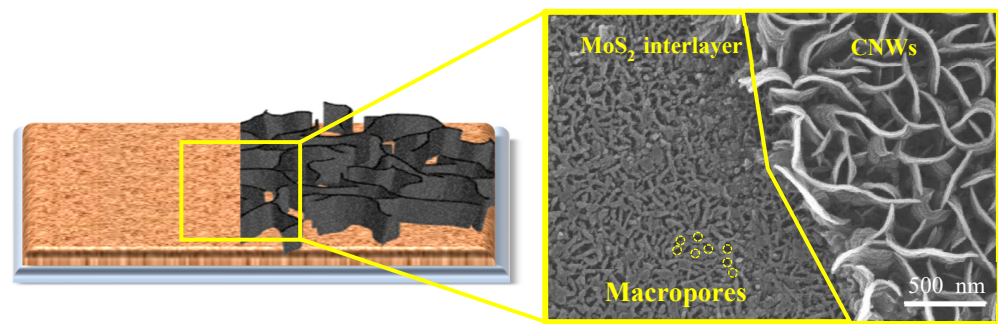
whereas the MoS<sub>2</sub> interlayer grew to 750 nm. The morphological characteristics of CNW vary under the influence of the MoS<sub>2</sub> interlayer, and this variation can be attributed to the interaction between sulfur or molybdenum atoms on the MoS<sub>2</sub> surface and carbon atoms in the graphene sheet. A graphene sheet with a low defect density is formed in the growth of the initial process by van der Waals forces generated at the interface, and it grows with a sharp-shaped edge. A stoichiometric analysis of the CNW/MoS<sub>2</sub> sample by EDS was performed and is shown in Figure 4. This result confirmed the existence of CNWs and MoS<sub>2</sub>, and also confirmed that the sample was successfully synthesized.

### 3.2. Raman Spectra

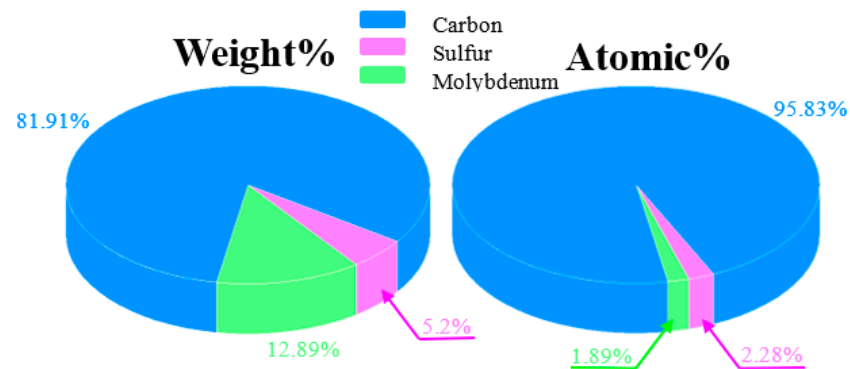
Figure 5a shows the results of the Raman spectroscopy analysis before and after annealing of the MoS<sub>2</sub> interlayer. E<sub>2g</sub><sup>1</sup>, showing in-plane vibrational characteristics, and A<sub>1g</sub>, showing interlayer vibrational characteristics, were observed. Compared to pristine MoS<sub>2</sub>, annealed MoS<sub>2</sub> exhibited a peak shift of approximately 11 cm<sup>−1</sup> in the E<sub>2g</sub><sup>1</sup> mode from 351 cm<sup>−1</sup> to 362 cm<sup>−1</sup> [19]. The blue shift phenomenon is due to the increase in the van der Waals forces between the MoS<sub>2</sub> interlayers during the annealing process. When the thickness of the interlayer decreases, the distance between E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> decreases [20]. Results of the Raman spectrum analysis of the CNW are shown in Figure 5b. Defects in graphite or amorphous carbon cause a high intensity D-peak, and this was observed at 1345 cm<sup>−1</sup> [21]. The presence of the MoS<sub>2</sub> interlayer decreases the D-peak of CNW (Figure 5c). In addition, there is a G-peak at about 1592 cm<sup>−1</sup>, which is commonly found in carbon-based materials, and appears due to sp<sup>2</sup> bonding or the effect of graphitization [22]. The peak observed at around 2686 cm<sup>−1</sup> is a 2D peak, indicating the double resonance of the pi-bond. When the number of layers of graphene is relatively low, the relatively higher intensity peaks appear. The CNW exhibits low-intensity peaks due to the existence of multi-layer graphene [23].



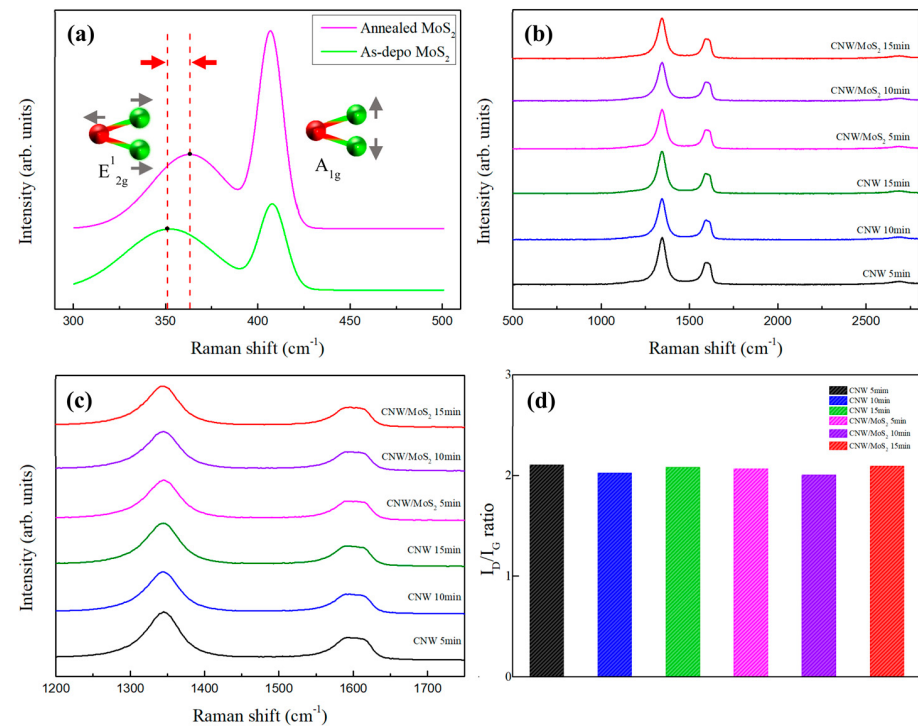
**Figure 2.** Cross-sectional FE-SEM image of a CNW: (a) CNW grown for 10 min on a glass substrate; (b) CNW grown for 10 min on the MoS<sub>2</sub> interlayer and the corresponding magnified image.



**Figure 3.** Schematic illustration and corresponding FE-SEM surface images including MoS<sub>2</sub>, the CNW and the interface.



**Figure 4.** EDS component analysis of the CNW/MoS<sub>2</sub> sample.



**Figure 5.** Raman spectra of CNWs and MoS<sub>2</sub>: (a) Raman spectroscopic analysis results before and after annealing of the MoS<sub>2</sub> interlayer; (b) Raman spectroscopic analysis results of each CNW sample grown under various conditions and (c) the corresponding high-resolution Raman spectrum with D and G peaks enlarged; and (d) I<sub>D</sub>/I<sub>G</sub> ratio of each CNW sample grown under various conditions.

#### 4. Conclusions

In summary, MoS<sub>2</sub>, a transition metal dichalcogenide material, was successfully synthesized using the RF magnetron sputtering system, while CNW, a carbon allotrope, was grown using the PECVD method. MoS<sub>2</sub> was used as an interlayer material, represents the key subject of this study. The surface density, pores diameter, and growth rate of CNW were changed, and results were characterized through SEM and EDS. Based on these results, it was confirmed that the MoS<sub>2</sub> interlayer is an innovative material that greatly affects the initial growth of CNW and consequently causes variation in its morphological characteristics. In addition, further studies have shown the possibility of application to various nanostructure growth.

**Author Contributions:** Conceptualization, C.K. and W.C.; formal analysis, C.K. and S.K.; investigation, K.K., B.H. and H.K.; writing—original draft preparation, C.K.; writing—review and editing, C.K.; visualization, C.K.; supervision, W.C. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20204030200080), as well as by a National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT). (No.2022R1A2C10097091131482092260101).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available in article.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

- Shi, H.; Wen, G.; Nie, Y.; Zhang, G.; Duan, H. Flexible 3D carbon cloth as a high performing electrode for energy storage and conversion. *Nanoscale* **2020**, *12*, 5261–5285. [[CrossRef](#)] [[PubMed](#)]
- Lee, S.; Kwon, S.; Kim, K.; Kang, H.; Ko, J.M.; Choi, W. Preparation of Carbon nanowall and Carbon Nanotube for Anode Material of Lithium-Ion Battery. *Molecules* **2021**, *26*, 6950. [[CrossRef](#)] [[PubMed](#)]
- Mori, S.; Ueno, T.; Suzuki, M. Synthesis of carbon nanowalls by plasma-enhanced chemical vapor deposition in a CO/H<sub>2</sub> microwave discharge system. *Diam. Relat. Mater.* **2011**, *20*, 1129–1132. [[CrossRef](#)]
- Kim, S.U.; Choi, W.S.; Lee, J.H.; Hong, B.U. Substrate temperature effect on the growth of carbon nanowalls synthesized via microwave PECVD. *Mater. Res. Bull.* **2014**, *58*, 112–116. [[CrossRef](#)]
- Zhang, L.X.; Sun, Z.; Qi, J.L.; Shi, J.M.; Hao, T.D.; Feng, J.C. Understanding the growth mechanism of vertically aligned graphene and control of its wettability. *Carbon* **2016**, *103*, 339–345. [[CrossRef](#)]
- Wu, Y.; Qiao, P.; Chong, T.; Shen, Z. Carbon Nanowalls Grown by Microwave Plasma Enhanced Chemical Vapor Deposition. *Adv. Mater.* **2022**, *14*, 64–67. [[CrossRef](#)]
- Choi, H.; Kwon, S.H.; Kang, H.; Kim, J.H.; Choi, W. Zinc-oxide-deposited Carbon Nanowalls for Acetone Sensing. *Thin Solid Films* **2020**, *700*, 137887. [[CrossRef](#)]
- Zhanga, J.; Khatria, I.; Kishia, N.; Mominuzzamanb, S.M.; Sogaa, T.; Jimbo, T. Low substrate temperature synthesis of carbon nanowalls by ultrasonic spray pyrolysis. *Thin Solid Films* **2011**, *519*, 4162–4165. [[CrossRef](#)]
- Kim, S.Y.; Lee, S.; Choi, W.; Jung, Y.H.; Lim, D.G. Growth and Resistance Properties of Carbon Nanowall According to the Variation of Reaction Gas. *J. KIEEME* **2014**, *27*, 217–220.
- Thi, M.T.; Kwon, S.; Kang, H.; Kim, J.H.; Yoon, Y.K.; Choi, W. Growth Properties of Carbon Nanowalls on Nickel and Titanium Interlayers. *Molecules* **2022**, *27*, 406.
- Wang, Q.H.; Zadeh, K.K.; Kis, A.; Coleman, J.N.; Strano, M.S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.* **2012**, *7*, 699–712. [[CrossRef](#)] [[PubMed](#)]
- Khan, M.; Kumar, S.; Mishra, A.; Tripathi, M.N.; Tripathi, A. Study of structural and electronic properties of few-layer MoS<sub>2</sub> film. *Mater. Today Proc.* **2022**, *57*, 100–105. [[CrossRef](#)]
- Shin, J.H.; Choi, Y.S.; Park, H.J. Remote Plasma-Induced Synthesis of Self-Assembled MoS<sub>2</sub>/Carbon Nanowall Nanocomposites and Their Application as High-Performance Active Materials for Supercapacitors. *Nanomaterials* **2022**, *12*, 1338. [[CrossRef](#)] [[PubMed](#)]
- Akikubo, K.; Kurahashi, T.; Kawaguchi, S.; Tachibana, M. Thermal expansion measurements of nano-graphite using high-temperature X-ray diffraction. *Carbon* **2020**, *169*, 307–311. [[CrossRef](#)]

15. Davami, K.; Shaygan, M.; Kheirabi, N.; Zhao, J.; Kovalenko, D.A.; Rummeli, M.H.; Opitz, J.; Cuniberti, G.; Lee, J.S.; Meyyappan, M. Synthesis and characterization of carbon nanowalls on different substrates by radio frequency plasma enhanced chemical vapor deposition. *Carbon* **2014**, *72*, 372–380. [[CrossRef](#)]
16. Quinlan, R.A.; Cai, M.; Outlaw, R.A.; Butler, S.M.; Miller, J.R.; Mansour, A.N. Investigation of defects generated in vertically oriented graphene. *Carbon* **2013**, *64*, 92–100. [[CrossRef](#)]
17. Serra, E.B.; Avetisyan, A.M.; Chaitoglou, S.; Rovira, R.A.; Alshaikh, I.; Suárez, F.P.; Bella, J.L.A.; Jawhari, T.; Pino, A.P.; Gyorgye, E. Temperature-modulated synthesis of vertically oriented atomic bilayer graphene nanowalls grown on stainless steel by inductively coupled plasma chemical vapor deposition. *Appl. Surf. Sci.* **2023**, *610*, 155530. [[CrossRef](#)]
18. Tzeng, Y.; Chen, W.L.; Wu, C.; Lo, J.Y.; Li, C.Y. The synthesis of graphene nanowalls on a diamond film on a silicon substrate by direct-current plasma chemical vapor deposition. *Carbon* **2013**, *53*, 120–129. [[CrossRef](#)]
19. Feng, J.; Fan, Y.; Zhao, H.; Zhang, Y. The First Principles Calculation on the Raman Spectrum and Optical Properties of the Defect Monolayer MoS<sub>2</sub>. *Braz. J. Phys.* **2021**, *51*, 493–498. [[CrossRef](#)]
20. Cicily Rigia, V.J.; Jayaraj, M.K.; Saji, K.J. Envisaging radio frequency magnetron sputtering as an efficient method for large scale deposition of homogeneous two dimensional MoS<sub>2</sub>. *Appl. Surf. Sci.* **2020**, *529*, 147158. [[CrossRef](#)]
21. Nong, J.; Wei, W.; Song, X.; Tang, L.; Yang, J.; Sun, T.; Yu, L.; Luo, W.; Li, C.; Wei, D. Direct growth of graphene nanowalls on silica for high-performance photo-electrochemical anode. *Surf. Coat. Technol.* **2022**, *624*, 423–432. [[CrossRef](#)]
22. Cancado, L.G.; Jorio, A.; Pimenta, M.A. Measuring the absolute Raman cross section of nanographites as a function of laser energy and clystallite size. *Phys. Rev. B* **2007**, *76*, 064304. [[CrossRef](#)]
23. Cancado, L.G.; Takai, K.; Endo, E.; Kim, Y.A.; Mizusaki, N.L.; Jorio, A.; Pimenta, M.A. Measuring the degree of stacking order in graphite by Raman spectroscopy. *Carbon* **2008**, *46*, 272–275. [[CrossRef](#)]