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Unbundling SWCNT Mechanically via Nanomanipulation Using AFM †

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Abstract: Carbon nanotubes (CNTs) are cylindrical nanostructures fabricated from carbon atoms that seem like seamless cylinders composed of rolled sheets of graphite. Owing to the unique properties of single-walled carbon nanotubes (SWCNTs), they are a promising candidate in various fields such as chemical sensing, hydrogen storage, catalyst support, electronics, nanobalances, and nanotubes. Because of their small size, large surface area, high sensitivity, and reversible behavior at room temperature, CNTs are ideal for measuring gas. They also show improved electron transfer when used as electrodes in electrochemical reactions and serve as solid media for protein immobilization on biosensors. SWCNTs can be metallic or semi-conductive, counting on their structural properties. In this study, an atomic force microscope (AFM) was used as a powerful tool to manipulate and disaggregate SWCNTs. By precisely controlling the AFM probe, it was possible to manipulate individual SWCNTs and separate them from the bundle structures. Next, the electrical transport of disaggregated SWCNTs was studied using the conductive atomic force microscope (cAFM) technique. Thus, current-voltage measurements on the unbundled branches of SWCNTs were carried out. Interestingly, these current-voltage measurements have allowed us to unravel the complex electrical characteristics of the nanotube bundle, which is a very crucial issue for gating effects as well as the resistance of the interconnects within carbon nanotube network devices.

Keywords: AFM; cAFM; SWCNT; nanomanipulation

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1. Introduction

A carbon nanotube (CNT) is a cylindrical structure of carbon atoms that can be viewed as seamless cylinders rolled up as layers of graphite for a single-walled carbon nanotube (SWCNT). Due to the outstanding properties SWNTs possess, researchers are interested in getting a deeper and wider insight into the physics behind this one-dimensional system; nevertheless, many novel applications were developed including chemical sensors, hydrogen energy storage, catalyst support [1–9], electronic devices [10–16], high-sensitivity nano-balance for nanoscopic particles, and nano-tweezers. CNTs have some advantages over other bulky materials; because of their small size with a larger surface area, high sensitivity, fast response, and reversibility at room temperature, they also serve as gas sensors. Depending on the chirality of SWCNTs, they could be metallic or semiconductors.

An atomic force microscope (AFM) is one of the scanning probe techniques. In contrast to electron microscopes, an AFM is capable of working in ambient [17,18], liquids [19–25], and gases. Imaging is not the only function of an AFM; it can be used for lithography, spectroscopy, and nanomanipulation. Few studies have been carried out on CNT manipulation using an AFM [26–29]. The unbundling of SWNTs has not yet been carried out using an AFM.

This work presents a study of unbundling the SWCNT by manipulating it using an AFM tip and measuring the electrical characteristics of the bundle and the unbundled branches, by using the AFM tip as a nanoprobe to measure the local voltage-current characteristics.

2. Materials and Methods

2.1. Materials

Chemical vapor deposition (CVD)-prepared SWCNTs in powder form, dichloroethane (DCE), isopropyl alcohol (IPA), and acetone were purchased from Sigma-Aldrich, Germany. All chemicals were used as received.

2.2. Preparation of SWCNT Thin-Film Samples

First, the SWCNT powder was dispersed in DCE with a concentration of 20 mg/L at room temperature using the HIELSCHER tip sonicator with a sonotrode of a 2 mm diameter and a power of 95 watts. In order to reduce the heat effect of sonication, the sonication was carried out in a pulse of 30 s, followed by 30 s with the sonicator turned off and repeated for 15 min. Then, the solution was centrifuged to eliminate the undispersed and giant particles. A drop of the solution was cast on a chip of SiO_2/Si with gold electrodes.

2.3. AFM Measurement

The Veeco Multimode V system was connected to the Nanonis controller for performing AFM measurements (Veeco, USA/Nanonis, Specs, Switzerland). All experiments were conducted at room temperature under ambient pressure, utilizing a doped diamond tip (Nanosensors DT-NCHR, Nanoworld AG, Switzerland).

To begin, the sample was scanned in non-contact mode to locate a bundle connected to the gold electrode. Once such a bundle was identified, the AFM operating mode was switched to the contact mode. To ensure gentle handling and prevent any mechanical damage or cutting of the bundle, a soft approach strategy was adopted. The force of the cantilever was controlled to be 100 pN during the soft approach.

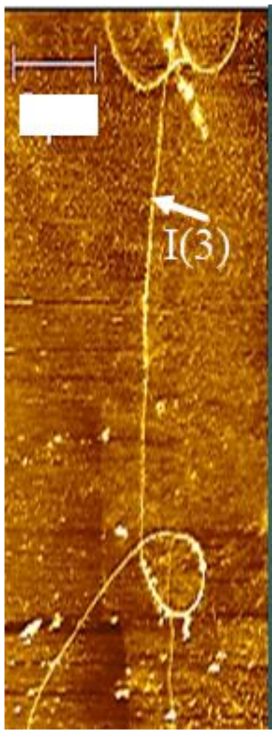
Upon approaching the bundle, a 100 nm $\times$ 100 nm mesh with 64 data points was established to scan the cantilever's deflection, confirming contact with the bundle. Subsequently, the tip was accurately positioned on the bundle, and a relatively larger force was applied to split the tubes.

Next, a force of 100 nN was applied and the tip was dragged along a line perpendicular to the bundle, simultaneously applying a potential of 1.0 V to the tip. We repeated this process for different trials, ensuring that after each trial, the tip was cleaned on the gold electrode. This was carried out for two purposes: first, to enable the scanning of the surface and reconstruct a topographical image; and second, to verify its electrical conductivity.

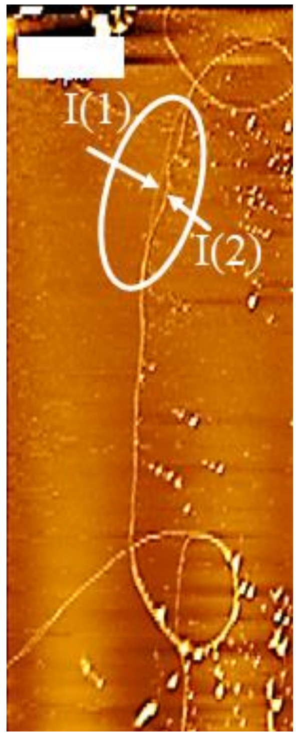
For the electrical measurements, a voltage was sourced to the AFM tip, and the current was drained from the gold electrode through the CNT tube/bundle. The voltage was swept from -0.5 to 0.5 V, and the corresponding current values were recorded to establish the I–V relationship.

3. Results and Discussion

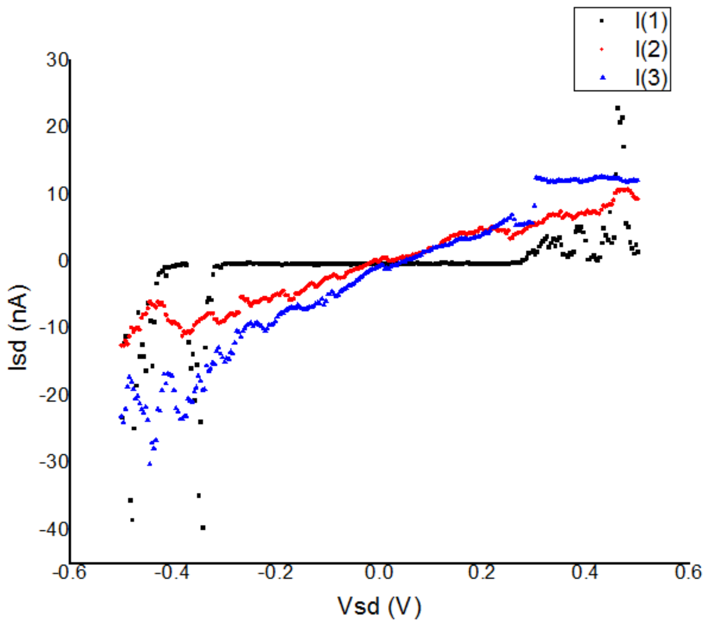
As previously mentioned, we utilized the non-contact mode to scan the sample and identify a bundle connected to the gold electrode. In Figure 1a, the bundle shown is connected to the electrode on one side and free on the other side. That was confirmed by measuring the electrical contact on it at point I(3) (Figure 1a), which is presented in the voltage-current curve shown in Figure 1c.



(**a**)



(**b**)



(**c**)

Figure 1. Topography images of SWNT deposited on SiO_2/Si substrate (white scale bars have a length of 3 µm): (**a**) SWNT before manipulation; (**b**) SWNT after manipulation; (**c**) voltage—current measurements on the assigned branches before and after manipulation of a nanotube bundle. The manipulation has unmasked two different characteristics, which can be assigned to a semiconducting branch, I(1), and a metallic branch, I(2), within the nanotube bundle.

Subsequently, the mode was switched to the contact mode using the gentle approach described earlier. With the help of the mesh, the electrical properties of the bundle at the specific point where the bundle was later split were measured, as depicted in Figure 1c (the blue curve).

During this manipulation process, the bundle was successfully split into two branches, as illustrated in Figure 1b. The unbundled branches were then subjected to electrical characterization (Figure 1c) by measuring the I–V curve for both branches at the points indicated by the arrows in Figure 1b.

Based on the electrical characterization, it was inferred that one branch exhibited metallic/semimetal characteristics, evident from the linearity of the red curve in Figure 1c. On the other hand, the other branch of the split bundle displayed characteristics similar to that of a diode, as seen in the black curve in Figure 1c.

4. Conclusions

An AFM has emerged as a potent and versatile tool for precisely manipulating and assembling single-walled carbon nanotubes (SWCNTs). Its remarkable capability to position SWCNTs with nanometer-level accuracy holds tremendous promise for advancing nanoelectronic devices and other nanoscale applications. Our research demonstrated the mechanical manipulation of carbon nanotubes using an AFM tip, achieved by applying both mechanical force and electrical potential to the tip. Employing the contacting mode of an AFM, the carbon nanotube bundle was successfully split into distinct branches. Subsequently, local electrical transport measurements were conducted on the bundle, both before and after splitting, utilizing the conductive mode of an AFM with the tip in contact with the CNT. The electrical measurements revealed distinguishable characteristics between metallic and semiconducting tubes.

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References

1. Alkallas, F.H.; Alghamdi, S.M.; Rashed, E.A.; Trabelsi, A.B.G.; Nafee, S.S.; Elsharkawy, W.B.; Alsubhe, E.; Alshreef, S.H.; Mostafa, A.M. Nanocomposite Fe3O4-MWCNTs based on femtosecond pulsed laser ablation for catalytic degradation. *Diam. Relat. Mater.* **2023**, *140*, 110445. [CrossRef]
2. Alrebdi, T.A.; Ahmed, H.A.; Alkallas, F.H.; Mwafy, E.A.; Trabelsi, A.B.G.; Mostafa, A.M. Structural, linear and nonlinear optical properties of NiO nanoparticles–multi-walled carbon nanotubes nanocomposite for optoelectronic applications. *Radiat. Phys. Chem.* **2022**, *195*, 110088. [CrossRef]
3. Al-Kadhi, N.S.; Pashameah, R.A.; Ahmed, H.A.; Alrefaee, S.H.; Alamro, F.S.; Faqih, H.H.; Mwafy, E.A.; Mostafa, A.M. Preparation of NiO/MWCNTs nanocomposite for the removal of cadmium ions. *J. Mater. Res. Technol.* **2022**, *19*, 1961–1971. [CrossRef]
4. Altowyan, A.S.; Toghan, A.; Ahmed, H.A.; Pashameah, R.A.; Mwafy, E.A.; Alrefaee, S.H.; Mostafa, A.M. Removal of methylene blue dye from aqueous solution using carbon nanotubes decorated by nickel oxide nanoparticles via pulsed laser ablation method. *Radiat. Phys. Chem.* **2022**, *198*, 110268. [CrossRef]
5. Alamro, F.S.; Mostafa, A.M.; Ahmed, H.A.; Toghan, A. Zinc oxide/carbon nanotubes nanocomposite: Synthesis, characterization and catalytic reduction of 4-nitrophenol via laser assistant method. *Surf. Interfaces* **2021**, *26*, 101406. [CrossRef]
6. Alamro, F.S.; Mostafa, A.M.; Abu Al-Ola, K.A.; Ahmed, H.A.; Toghan, A. Synthesis of Ag Nanoparticles-Decorated CNTs via Laser Ablation Method for the Enhancement the Photocatalytic Removal of Naphthalene from Water. *Nanomaterials* **2021**, *11*, 2142. [CrossRef]
7. Mwafy, E.A.; Gaafar, M.S.; Mostafa, A.M.; Marzouk, S.Y.; Mahmoud, I.S. Novel laser-assisted method for synthesis of SnO2/MWCNTs nanocomposite for water treatment from Cu (II). *Diam. Relat. Mater.* **2021**, *113*, 108287. [CrossRef]
8. Mwafy, E.A.; Mostafa, A.M. Tailored MWCNTs/SnO2 decorated cellulose nanofiber adsorbent for the removal of Cu (II) from waste water. *Radiat. Phys. Chem.* **2020**, *177*, 109172. [CrossRef]

9. Mwafy, E.A.; Mostafa, A.M.; Awwad, N.S.; Ibrahium, H.A. Catalytic activity of multi-walled carbon nanotubes decorated with tungsten trioxides nanoparticles against 4-nitrophenol. *J. Phys. Chem. Solids* **2021**, *158*, 110252. [CrossRef]
10. Sakaguchi, T.; Jeon, I.; Chiba, T.; Shawky, A.; Xiang, R.; Kauppinen, E.I.; Chiashi, S.; Park, N.-G.; Matsuo, Y.; Maruyama, S. Non-Doped and Unsorted Single-Walled Carbon Nanotubes as Carrier-Selective, Transparent and Conductive Electrode for Perovskite Solar Cells. *MRS Commun.* **2018**, *8*, 1058–1063. [CrossRef]
11. Jeon, I.; Xiang, R.; Shawky, A.; Matsuo, Y.; Maruyama, M. Single-Walled Carbon Nanotubes in Emerging Solar Cells: Synthesis and Electrode Applications. *Adv. Energy Mater.* **2019**, *9*, 1801312. [CrossRef]
12. Jeon, I.; Shawky, A.; Lin, H.S.; Seo, S.; Okada, H.; Lee, J.-W.; Pal, A.; Tan, S.; Anisimov, A.; Kauppinen, E.I.; et al. Controlled Redox of Lithium-ion Endohedral Fullerene for Efficient and Stable Metal Electrode-Free Perovskite Solar Cells. *J. Am. Chem. Soc.* **2019**, *141*, 16553–16558. [CrossRef] [PubMed]
13. Qian, Y.; Seo, S.; Jeon, I.; Lin, H.; Okawa, S.; Zheng, Y.; Shawky, A.; Anisimov, A.; Kauppinen, E.I.; Kong, J.; et al. MoS2-carbon nanotube heterostructure as efficient hole transporters and conductors in perovskite solar cells. *Appl. Phys. Express* **2020**, *13*, 075009. [CrossRef]
14. Lee, C.; Lee, S.-W.; Bae, S.; Shawky, A.; Devaraj, V.; Anisimov, A.; Kauppinen, E.I.; Oh, J.W.; Kang, Y.; Kim, D.; et al. Carbon Nanotube Electrode-Based Perovskite–Silicon Tandem Solar Cells. *Sol. RRL* **2020**, *4*, 2000353. [CrossRef]
15. Shawky, A.; Nam, J.-S.; Kim, K.; Han, J.; Yoon, J.; Seo, S.; Lee, C.S.; Xiang, R.; Matsuo, Y.; Lee, H.M.; et al. Controlled Removal of Surfactants from Double-Walled Carbon Nanotubes for Stronger p-Doping Effect and its Demonstration in Perovskite Solar Cells. *Small Methods* **2021**, *5*, 2100080. [CrossRef] [PubMed]
16. Seo, S.; Akino, K.; Nam, J.-S.; Shawky, A.; Lin, H.-S.; Nagaya, H.; Kauppinen, E.I.; Xiang, R.; Matsuo, Y.; Jeon, I.; et al. Multi-Functional MoO3 Doping of Carbon-Nanotube Top Electrodes for Highly Transparent and Efficient Semi-Transparent Perovskite Solar Cells. *Adv. Mater. Interfaces* **2022**, *9*, 2101595. [CrossRef]
17. Talyzin, A.V.; Luzan, S.; Anoshkin, I.V.; Nasibulin, A.G.; Kauppinnen, E.I.; Dzwilewski, A.; Kreta, A.; Jamnik, J.; Hassanien, A.; Lundstedt, A.; et al. Hydrogen-driven cage unzipping of C60 into nano-graphenes. *J. Phys. Chem. C* **2014**, *118*, 6504–6513. [CrossRef]
18. Kreta, A.; Pavlica, E.; Božič, M.; Bratina, G. Nanoscopic Roughness Characterization of Chitosan with Buried Graphene Oxide for Fuel Cell Application. *Eng. Proc.* **2023**, *31*, 26. [CrossRef]
19. Kreta, A.; Gaberšček, M.; Muševič, I. Time-resolved in situ electrochemical atomic force microscopy imaging of the corrosion dynamics of AA2024-T3 using a new design of cell. *J. Mater. Res.* **2021**, *36*, 79–93. [CrossRef]
20. Surca, A.K.; Kreta, A.; Mihelčič, M.; Gaberscek, M.; Rodošek, M. Benefits of Coupling of Electrochemical Technique with Either IR, Raman or AFM Technique in the Corrosion Investigation. *ECS Meet. Abstr.* **2017**, *MA2017-01*, 939. [CrossRef]
21. Surca, A.K.; Rodošek, M.; Kreta, A.; Mihelčič, M. Application of ex situ IR reflection-absorption, in situ Raman and in situ electrochemical AFM in the study of sol-gel protective coatings. In Proceedings of the EUROCORR 2017—The Annual Congress of the European Federation of Corrosion, 20th International Corrosion Congress and Process Safety Congress 2017, Prague, Czech Republic, 3–7 September 2017.
22. Surca, A.K.; Rodošek, M.; Kreta, A.; Mihelčič, M.; Gaberšček, M. In situ and ex situ electrochemical measurements: Spectroelectrochemistry and atomic force microscopy. In *Hybrid Organic-Inorganic Interfaces: Towards Advanced Functional Materials*; Delville, M.-H., Ed.; Wiley-VCH: Hoboken, NJ, USA, 2018; pp. 793–837.
23. Kreta, A. Nanoscopic Study of Corrosion Dynamics and Properties of Anticorrosion Coatings on Copper and Aluminium Alloys = Nanoskopska Študija Korozijske Dinamike in Lastnosti Protikorozijskih Prevlek na bakru in Aluminijevih Zlitinah. Ph.D. Thesis, Mednarodna Podiplomska šola Jožefa Stefana, Ljubljana, Slovenia, 2017. [CrossRef]
24. Kaker, B.; Hribernik, S.; Mohan, T.; Kargl, R.; Kleinschek, K.S.; Pavlica, E.; Kreta, A.; Bratina, G.; Lue, S.J.; Božič, M. Novel Chitosan-Mg(OH)2-Based Nanocomposite Membranes for Direct Alkaline Ethanol Fuel Cells. *ACS Sustain. Chem. Eng.* **2019**, *7*, 19356–19368. [CrossRef]
25. Kreta, A.; Hočevar, S.B. An In Situ AFM Study of Electrochemical Bismuth Film Deposition on a Glassy Carbon Substrate Electrode Using a Low Concentration of Bismuth Ions. *Eng. Proc.* **2023**, *31*, 27. [CrossRef]
26. Kashiwase, Y.; Ikeda, T.; Oya, T.; Ogino, T. Manipulation and soldering of carbon nanotubes using atomic force microscope. *Appl. Surf. Sci.* **2008**, *254*, 7897–7900. [CrossRef]
27. Ju, D.; Zhang, Y.; Li, R.; Liu, S.; Li, L.; Chen, H. Mechanism-independent manipulation of single-wall carbon nanotubes with atomic force microscopy tip. *Nanomaterials* **2020**, *10*, 1494. [CrossRef] [PubMed]
28. Yang, S.C.; Qian, X. Controlled manipulation of flexible carbon nanotubes through shape-dependent pushing by atomic force microscopy. *Langmuir* **2013**, *29*, 11793–11801. [CrossRef] [PubMed]
29. Hertel, T.; Martel, R.; Avouris, P. Manipulation of individual carbon nanotubes and their interaction with surfaces. *J. Phys. Chem. B* **1998**, *102*, 910–915. [CrossRef]