

Article

Carbon Nanotubes Grown Using Solid Polymer Chemical Vapor Deposition in a Fluidized Bed Reactor with Iron(III) Nitrate, Iron(III) Chloride and Nickel(II) Chloride Catalysts

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Abstract: In this study, multi-walled carbon nanotubes (MW-CNT) were successfully synthesized using a chemical vapor deposition-fluidized bed (CVD-FB), with 10% hydrogen and 90% argon by volume, and a reaction temperature between 750 and 850 °C in a specially designed three-stage reactor. A solid state of polyethylene (PE) was used as a carbon source and iron(III) nitrate, iron(III) chloride, and nickel(II) chloride were used as catalysts. Scanning and transmission electron microscopy and Raman spectrum analysis were used to analyze and examine the morphology and characteristics of the CNTs. A thermogravimetric analyzer was used to determine the purification temperature for the CNTs. Experimental results showed that the synthesis with iron-based catalysts produced more carbon filaments. Nickel(II) chloride catalysis resulted in the synthesis of symmetrical MW-CNTs with diameters between 30 and 40 nanometers. This catalyst produced the best graphitization level (I_D/I_G) with a value of 0.89. Excessively large particle size catalysts do not cluster carbon effectively enough to grow CNTs and this is the main reason for the appearance of carbon filaments.

Keywords: solid PE; chemical vapor deposition-fluidized bed; MW-CNT; graphitization; carbon filaments

1. Introduction

Carbon nanotubes (CNT) were discovered accidentally when Iijima (Japan) was using Direct-current (DC)-arc discharge to study Fullerene C_{60} , and his paper in Nature in 1991 drew world-wide attention [1]. CNTs are hollow tubes with walls formed of the graphite layers with sp^2 bonding. CNTs have a mesh-like conjugated π bond, π electron cloud, and hollow tube. These characteristics confer mechanical, electrical, optical, and chemical properties to the nanotubes, which include high strength, a large surface area, and high heat and electrical conductivity. CNTs have widely been applied in nano machinery components, storage of hydrogen materials, and field emission display components. Many industries have taken advantage of these nanotubes as an important material that has overcome the material size barrier between the micro and nano levels.

CNTs present many promising future applications such as superior emitters for new X-ray imaging applications [2], electrodes with excellent capacitance [3], improvements in fuel cells to boost performance and efficiency [4], CNT/MgO layer for the alternate current-plasma display panel (AC PDP) protection [5], CNT-based composite film with improved film function [6], using its magnetism for the exploration and induction of cancer cells [7], lithium ion battery applications [8], and as an adsorbent or disinfectant material for removing microbes from drinking water [9].

There have been many studies being carried out on CNTs and related problems, especially on the methods for their production. The examples include using natural cotton fiber to synthesize CNT [10], traditional arc discharge methods [11], thermal decomposition, and plasma enhanced chemical vapor deposition (PECVD). Recently, Wei et al. proposed a combination of a fluidized bed with CVD to create a CVD-fluidized bed (CVD-FB) that can be used for continuous output. In this reaction, the size of the CNTs can be easily controlled [12–15]. In addition to these methods, our team has also successfully synthesized CNTs using polycarbosilane (PCS) by the CVD-FB method [16].

However, the most of these methods to produce CNTs were used gaseous hydrocarbons such as methane or ethane, posing a considerable risk during use, store, and transport. In view of this, several studies focused on the use of a solid polymer as the carbon source [16–22]. In manufacturing process, a fluidized bed reactor (FBR) is easy to scale up production. Thus, we use CVD-FBR method to synthesize CNTs from solid state plastics. We explored how the use of different catalysts affects carbon nano-tube production and investigated a multi-step purification process for the prepared CNTs using pre-heating and acid washing. Transmission electron microscopy (TEM) was used to observe the microstructure of the resulting CNTs and the Raman spectrum analysis was used to determine the level of graphitization. We also investigated the effects of the purification process. The purpose of this study is that we hope we can realize eco-efficient economy concept of waste plastics to reuse them and make high value of them.

2. Materials and Methods

2.1. Materials, Methods and Equipment

For the experiments, we designed a fluidized bed reactor (in Figure 1) to which reactants can easily be added and was also easy to clean. The reactor is made mainly of stainless steel, with an internal diameter of 2.1 cm, and a total length of 40 cm. There is a distributor in the center of the reactor made of a porous stainless steel plate to ensure even gas distribution.

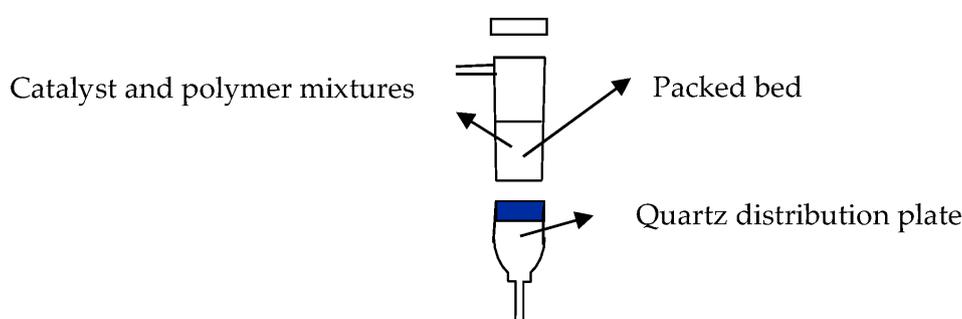


Figure 1. Schematic diagram of the three-section reactor.

There are two heaters, one above the other. The temperature used at the upper level is 750 °C and at the lower level is 850 °C. A higher temperature at the bottom ensures proper pyrolysis of the polymer and efficient catalytic reduction. The upper-level temperature of 750 °C is conducive to the production of carbon tubes. The fluidized gas is a mixture of 10% hydrogen and 90% argon by volume. The experimental setup is shown in Figure 2.

Experiments were conducted using three types of catalyst: iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Showa, Tokyo, Japan), iron(III) chloride (FeCl_3 , Showa, Tokyo, Japan), and nickel(II) chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Showa, Tokyo, Japan). In order to ensure that the catalysts were mole number equivalent, 9.19 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 3.68 g of FeCl_3 , and 5.40 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, were weighed into three flasks to which 100 mL of alcohol was added. Polyethylene (PE) powder with a particle size of 180 mm (25 g) was added to each flask and ultrasonic agitation was used to ensure proper suspension of the particles.

Alcohol was evaporated and the residue was dried in an oven at 60 °C for 48 h, after which it was ground into a powder to prepare for the reaction process.

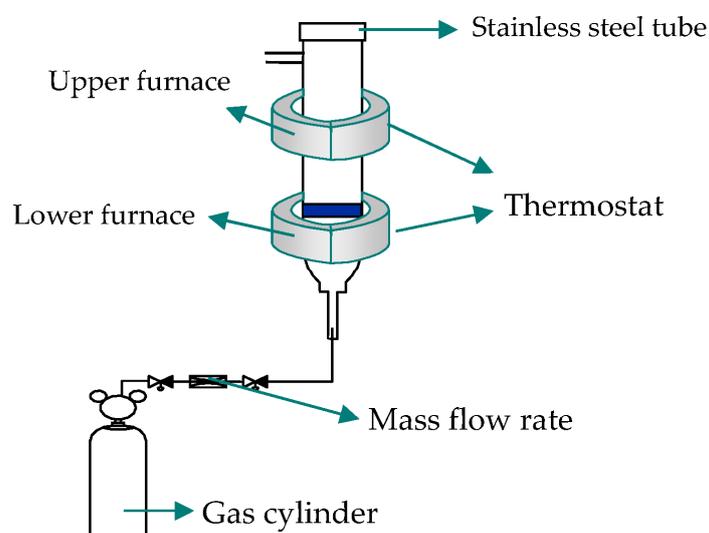


Figure 2. Schematic diagram of the chemical vapor deposition-fluidized bed reactor (CVD-FBR) used in this study.

2.2. Experimental Method

Before the reaction, a small amount of quartz wool was placed on the distributor, and nickel pellets with the size 0.3175 cm were used as bed filler to a height of about 2 to 3 cm. The prepared catalyst with polymer powder was added and the carrier gas was introduced at a flow rate of 750.0 cc/min with heating. After the system had fluidized and was stable the heat was increased to achieve the reaction temperature of 750 °C on the upper level and 850 °C below.

2.3. Purification Method

For purification, we used the method developed by Jinyong [23]. The prepared CNT powder was suspended in a 3% solution of dodecyl sulfonic acid sodium salt (SDS) and ultrasound agitation was carried out for 2 h. The suspension was passed through a thin nylon membrane filter with a pore size of 0.45 μm . The residue was dried at 60 °C and a thermogravimetric analyzer (TGA; Rigaku Thermo Plus TG8120; Rigaku Corporation, Tokyo, Japan) was used to test the metal catalyst oxidation temperature of the prepared CNT. Based on the TGA analytical result, CNT obtained from iron(III) nitrate, iron (II) chloride, and nickel(II) sulfate were all separately processed at 380, 400, and 420 °C for 2 h, respectively and concentrated hydrochloric acid was used for the acid wash. Finally, the product was washed with distilled water, filtered through a thin film and dried to obtain the purified CNT preparation.

2.4. Analytical Method

The morphology of CNTs obtained through FB-CVD reaction and multiple purification procedures was examined by scanning electron microscope (SEM; JEOL JSM-6500F; JEOL Ltd., Tokyo, Japan) and high-resolution transmission electron microscope (HR-TEM; Philips, FEI Tecnai F20 G2; Hillsboro, OR, USA). The transmission electron microscope (TEM) allowed visualization of the walls of the carbon nanotubes and a Raman spectrum analyzer was used to determine the level of graphitization.

3. Results

3.1. Carbon Nanotubes (CNT) Preparation

Figure 3 shows an SEM image of CNTs obtained by using the different catalysts. Figure 3a shows the initial product obtained with iron(III) nitrate catalyst. Although some CNTs can be seen, most of the material is amorphous carbon residue. Figure 3b shows the initial product produced with the iron(III) chloride catalyst. The result reveals the good quantity of CNT clusters, even though most of the product is still carbon residue. Figure 3c shows the initial product produced with nickel(II) chloride catalyst. The nickel(II) chloride product also shows CNTs. However, in comparison with the other two figures, it shows that the products obtained by the nickel(II) chloride catalyst have a structure similar to products obtained by the iron(III) chloride catalyst. CNTs are concentrated and contain large quantities of impurities. The results obtained using these three different catalysts showed that the solid state polymer raw material can be used in a chemical vapor deposition-fluidized bed reactor to successfully produce CNTs.

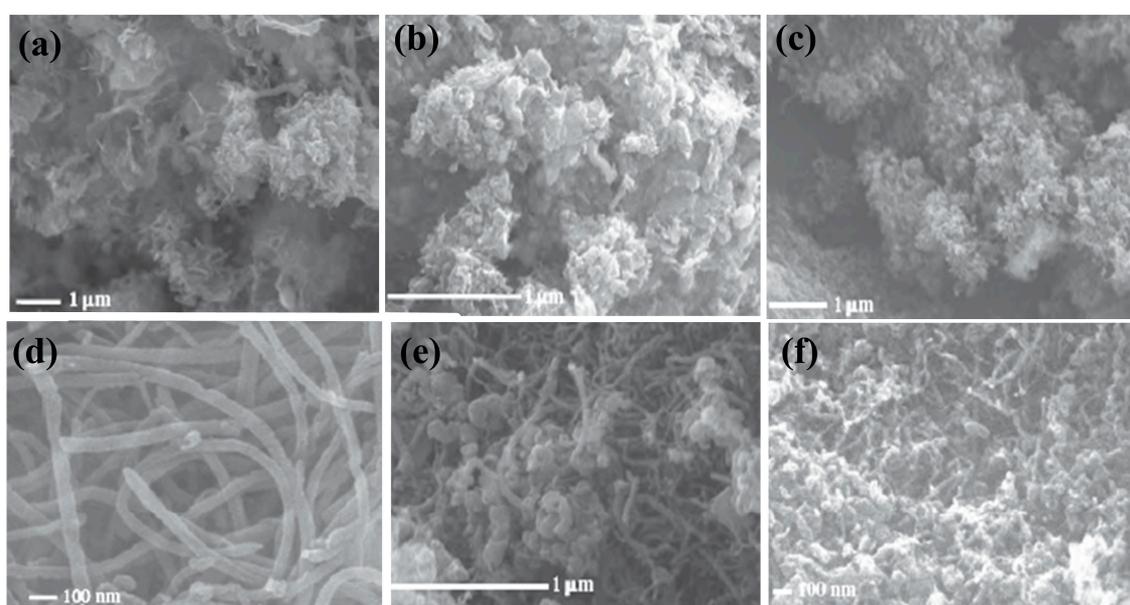


Figure 3. The initial product synthesized by using (a) iron(III) nitrate; (b) iron(III) chloride; and (c) nickel(II) chloride catalysts; purified product obtained by (d) iron(III) nitrate; (e) iron(III) chloride; and (f) nickel(II) chloride catalysts.

3.2. CNT Purification

Figure 4 shows the TGA analysis of CNTs obtained by using different catalysts. Ramesh [24] indicated that the weight loss, below 400 °C, is caused by the oxidation of amorphous carbon residue, while weight gain around 400 °C is caused by the oxidation of metal catalysts. Weight gain from 500 to 700 °C is from single wall CNT oxidation. Jinyong [23] prepared CNTs in a 3% sodium dodecyl sulfate (SDS) solution using ultrasound agitation. The clustered carbon tubes were separated before heat treatment was used. An amorphous carbon residue was oxidized and removed, and the initially distributed metal catalyst was also oxidized. A volume expansion allowed the metal catalyst to break through the carbon tube wall and the acid wash removed the metal catalysts and achieved effective purification. Based on the TGA results, we processed the nitrate catalyst produced CNTs at 380 °C for 2 h. We theorize that the scale-like objects are metal oxidized products since, at present, we have not analyzed this product in detail. Carbon tubes were taken heat treatment and soaked in concentrated hydrochloric acid. After several minutes of ultrasound agitation, the tubes were cleaned. Figure 3d

shows a SEM image of the iron(III) nitrate system after acid washing. The saw tooth objects have disappeared after heat processing, leaving the CNTs clearly visible. This method was also used to purify the CNTs produced with iron(III) chloride catalyst and nickel(II) chloride catalyst at 400 and 420 °C, respectively. Figure 3e,f show the SEM images of the samples. CNTs can be clearly observed in these images indicating that this method can effectively purify CNTs.

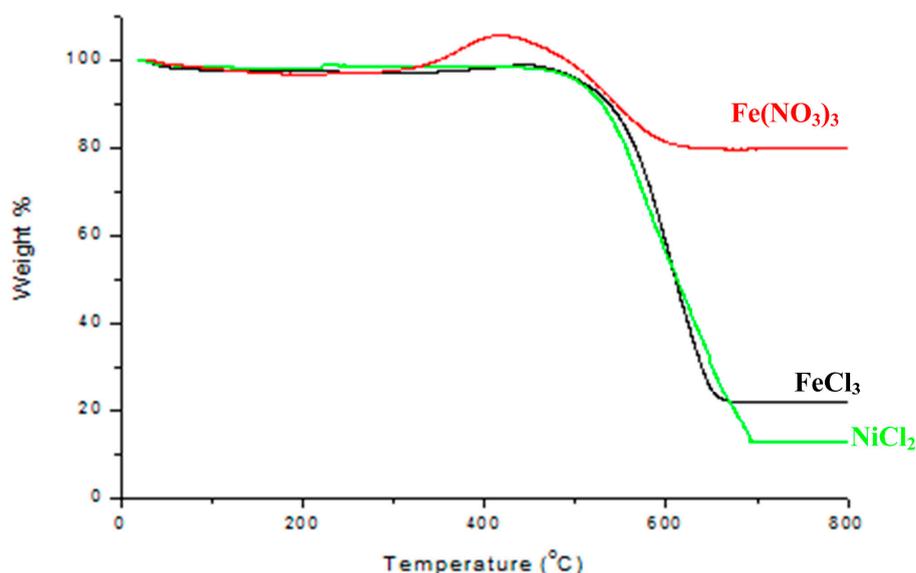


Figure 4. The thermogravimetric analyzer (TGA) analysis of carbon nanotubes obtaining different catalysts.

4. Discussion

Figure 4d–f show quite different tube diameter distribution after the purification. The TEM images of the samples obtained with the iron(III) nitrate (Figure 5a) and iron(III) chloride (Figure 5b) catalysts also show these differences. The image in Figure 6a shows many thick and solid carbon filaments produced in a process using this catalyst. Figure 6b is a typical multi-walled CNTs (MW-CNTs) structure with the diameters of about 30 to 40 nm. The iron(III) nitrate catalyst system produced few CNTs and the iron(III) chloride catalyst system resulted in a mix of large carbon filaments and CNTs. Table 1 shows a comparison of the carbon tubes produced using these different catalysts. The iron based catalysts produced large carbon filaments, while the nickel(II) chloride catalyst produced more complete MW-CNTs.

Table 1. Comparison of carbon tubes prepared with different catalysts. CNTs: carbon nanotubes.

Catalyst	Diameter (nm)	I _D /I _G	Note
Fe(NO ₃) ₃	60~100	0.99	Most of the products are carbon tube with a large diameter. It is difficult to find CNTs.
FeCl ₃	40~80	0.95	Most of the products are carbon tube with a large diameter. Only a few of them are mixed with multi-wall CNTs.
NiCl ₂	30~40	0.89	CNTs with symmetric tube-walls were obtain.

Figure 5a shows a large carbon filament with the end covered by a large particle of the catalyst. The reason why iron catalyst systems so easily produce large catalyst granules is not clear. A possibility is that in a hydrogen atmosphere, the decomposition temperature of PE is not very close to the temperature of the catalyst reduction to metal particles. This quickly nucleates the catalyst particles and they grow to form larger particles. Furthermore, when the PE and metal salts break down,

many different gases are produced, and this makes this a multi-environment experiment. Future work is needed to resolve this problem.

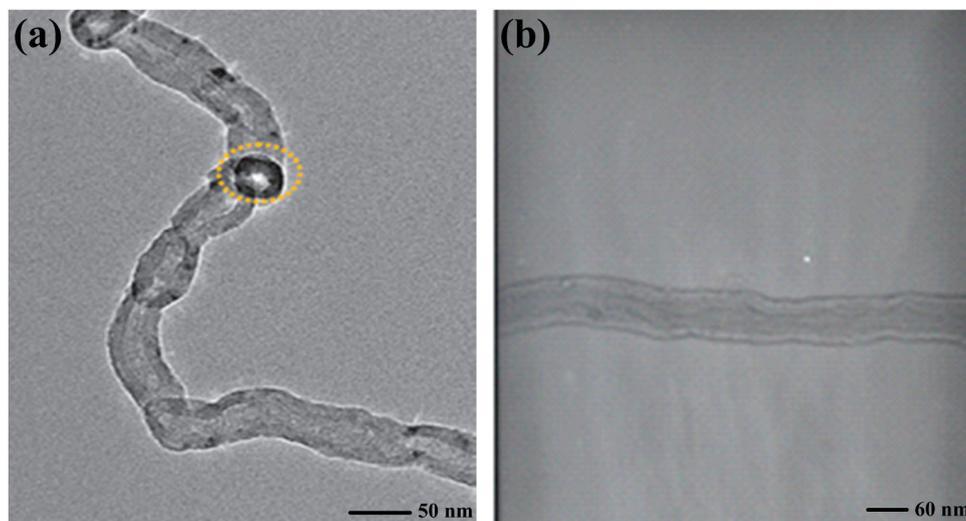


Figure 5. (a) Thickly walled carbon filament produced using iron(III) chloride catalyst (yellow dotted circle); and (b) the nickel(II) chloride catalyst produced nanotubes with symmetrical walls.

Figure 6 shows the Raman analysis (Renishaw; inVia Raman microscope; Sheffield, UK) of the products obtained with the different catalysts. The 1340 cm^{-1} absorption peak is in the D-band, which is a characteristic of the defective tube walls. The 1570 to 1610 cm^{-1} peak is in the G-band, being the characteristics of carbon tube graphitization [17,25]. A strong bending can easily produce pentacarbon or heptacarbon rings, which will increase the strength of the D-band, making the occurrence of all D-bands significantly. I_D/I_G is generally used to inspect CNT quality. However, the iron(III) nitrate and iron(III) chloride catalyzed products had large amounts of carbon filament and no CNTs. In the present case, the I_D/I_G ratio values could not be used and served only as a reference and the I_D/I_G ratio value of 0.89 was meaningful only in the nickel(II) chloride catalyzed product.

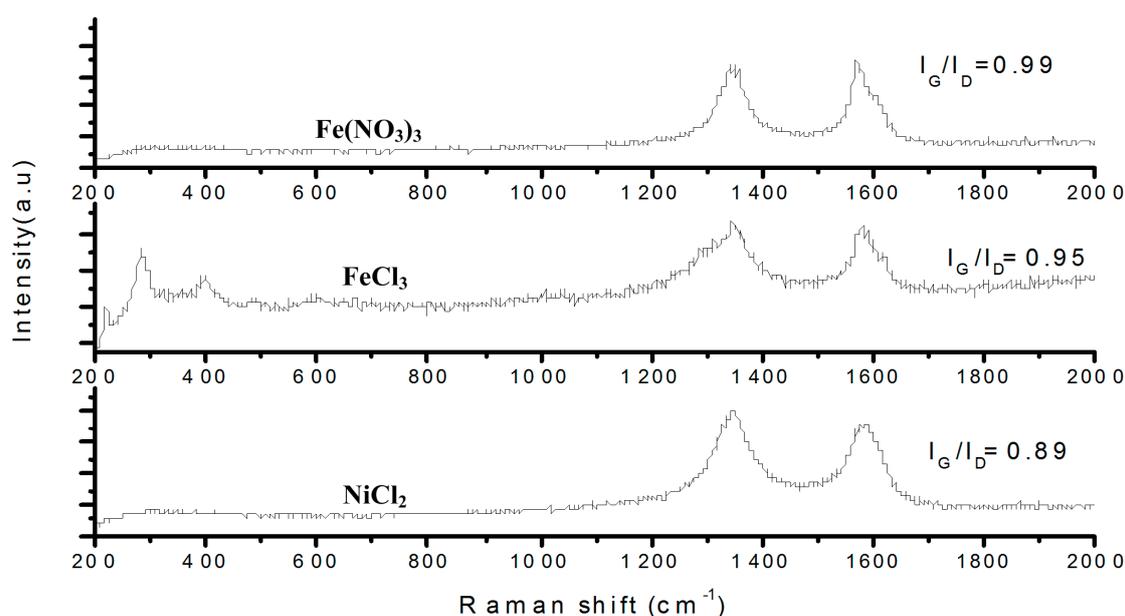


Figure 6. Raman analysis of CNT prepared with different catalysts.

In addition, CNTs obtained using CVD with a fluidized bed do not grow in any specific direction because the particles in the system are disturbed by easily occurring turbulence and bending.

5. Conclusions

We successfully produced CNTs using the CVD-FBR method and used heat treatment and acid washing to remove most of the impurities. The purified products obtained with the iron salt catalysts had great quantity of large carbon filaments. The cause of this can be attributed to the presence of large catalyst particles. The nickel catalyst produced MW-CNTs with symmetrical tube walls. Since the iron salt system produced large carbon filaments, the I_D/I_G ratio value was useful only for reference and the I_D/I_G ratio value of 0.89 was meaningful only in case of the nickel(II) chloride catalyst.

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

References

1. Iijima, S. Helical microtubules of graphitic carbon. *Nature* **1991**, *354*, 56–58. [[CrossRef](#)]
2. Dokania, A.K.; Chen, Z.; Rupesinghe, N.; Wirth, T.; Bachmann, P.K. Improved field emission of CNTs on heated substrate for medical X-ray imaging application. In Proceedings of the Technical Digest of the 25th International Vacuum Nanoelectronics Conference, Jeju Island, Korea, 9–13 July 2012; pp. 124–125.
3. Jiang, J.; Li, L.; Liu, Y.; Liu, S.; Xu, M.; Zhu, J. Uniform implantation of CNTs on total activated carbon surfaces: A smart engineering protocol for commercial supercapacitor applications. *Nanotechnology* **2017**, *28*. [[CrossRef](#)] [[PubMed](#)]
4. Mukherjee, S.; Bates, A.; Lee, S.C.; Lee, D.H.; Park, S. A review of the application of CNTs in PEM fuel cells. *Int. J. Green Energy* **2015**, *12*, 787–809. [[CrossRef](#)]
5. Deng, J.; Wang, X.J. Application of CNTs functional layer in AC plasma display panels. *J. Univ. Electron. Sci. Technol. China* **2016**, *45*, 151–154.
6. Ma, L.; Dong, X.; Chen, M.; Zhu, L.; Wang, C.; Yang, F.; Dong, Y. Fabrication and water treatment application of carbon nanotubes (CNTs)-based composite membranes: A review. *Membranes* **2017**, *7*. [[CrossRef](#)] [[PubMed](#)]
7. Szymanski, L.; Kolacinski, Z.; Raniszewski, G.; Gryska, E. CNTs synthesis on steel strip a in microwave plasma reactor for medical application. In Proceedings of the 15th International Conference on Nanotechnology (IEEE-NANO 2015), Rome, Italy, 27–30 July 2015; pp. 1062–1065.
8. Li, L.; Yang, H.; Zhou, D.; Zhou, Y. Progress in application of CNTs in lithium-ion batteries. *J. Nanomater.* **2014**, *2014*. [[CrossRef](#)]
9. Liu, S.; Zheng, X.; Yang, Y.; Liu, J.; Lie, J. The removal and inhibitory effect of CNTs on model viruses. *Mater. Sci. Forum* **2013**, *743–744*, 402–408. [[CrossRef](#)]
10. Lin, Z.G.; Gao, F.; Li, K.; Wang, Z.; Jahan, M. Using natural cotton fibers to synthesize carbon nanotubes and electromagnetic wave absorption properties. *Mater. Sci. Eng. B* **2017**, *24*, 61–68.
11. Zhao, T.; Ji, X.; Jin, W.; Yang, W.; Li, T. Hydrogen storage capacity of single-walled carbon nanotube prepared by a modified arc discharge. *Fuller. Nanotub. Carbon Nanostruct.* **2017**, *25*, 355–358. [[CrossRef](#)]
12. Ci, L.; Wei, B.; Liang, J.; Xu, C.; Wu, D. Preparation of carbon nanotubules by the floating catalyst method. *J. Mater. Sci. Lett.* **1999**, *18*, 797–799. [[CrossRef](#)]
13. Chen, C.C.; Chen, S.W. Nickel and copper deposition on Al_2O_3 and SiC particulates by using the chemical vapor deposition-fluidized bed reactor technique. *J. Mater. Sci.* **1997**, *32*, 4429–4435. [[CrossRef](#)]
14. Yen, Y.W.; Chen, S.W. Ni and Cu deposition on fine alumina particles by using the chemical vapor deposition-circulation fluidized bed reactor. *J. Mater. Sci.* **2000**, *35*, 1439–1444. [[CrossRef](#)]

15. Qian, W.; Liu, T.; Wang, Z.; Wei, F.; Li, Z.; Luo, G.; Li, Y. Production of hydrogen and carbon nanotubes from methane decomposition in a two-stage fluidized bed reactor. *Appl. Catal. A* **2004**, *260*, 223–228.
16. Chung, Y.H.; Jou, S. Carbon nanotubes from catalytic pyrolysis of polypropylene. *Mater. Chem. Phys.* **2005**, *92*, 256–259. [[CrossRef](#)]
17. Yen, Y.W.; Huang, M.D.; Lin, F.J. Synthesize carbon nanotubes by a novel method using chemical vapor deposition-fluidized bed reactor from solid-stated polymers. *Diam. Relat. Mater.* **2008**, *17*, 567–570. [[CrossRef](#)]
18. Jianh, Z.; Song, R.; Bo, W.; Lu, J.; Tang, T. Polypropylene as a carbon source for the synthesis of multi-walled carbon nanotubes via catalytic combustion. *Carbon* **2007**, *45*, 449–458.
19. Cesano, F.; Bertarione, S.; Scarano, D.; Spoto, G.; Zecchina, A. Designing of carbon nanofilaments-based composites for innovative applications. *Diam. Relat. Mater.* **2009**, *18*, 979–983. [[CrossRef](#)]
20. Yang, Z.; Zhang, Q.; Luo, G.; Huang, J.Q.; Zhao, M.Q.; Wei, E. Coupled process of plastics pyrolysis and chemical vapor deposition for controllable synthesis of vertically aligned carbon nanotube arrays. *Appl. Phys. A* **2010**, *100*, 533–540. [[CrossRef](#)]
21. Mishra, N.; Das, G.; Ansaldo, A.; Genovese, A.; Malerba, M.; Povia, M.; Ricci, D.; Fabrizio, E.M.D.; Zitti, E.F.D.; Sharon, M.; et al. Pyrolysis of waste Polypropylene for the synthesis of Carbon nanotubes. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 91–98. [[CrossRef](#)]
22. Jagadale, P.; Sharon, M.; Kalita, G.; Mahmud, N.; Sharon, N.M.M. Carbon nano material synthesis from polyethylene by chemical vapour deposition. *Adv. Mater. Phys. Chem.* **2012**, *2*, 1–10. [[CrossRef](#)]
23. Jinyong, L.; Yafei, Z. A simple purification for single-walled carbon nanotubes. *Phys. E* **2005**, *28*, 309–312.
24. Ramesh, P.; Okazaki, T.; Sugai, T.; Kimura, J.; Kishi, N.; Sato, K.; Ozeki, Y.; Shinohara, H. Purification and characterization of double-wall carbon nanotubes synthesized by catalytic chemical vapor deposition on mesoporous silica. *Chem. Phys. Lett.* **2006**, *418*, 408–412. [[CrossRef](#)]
25. Jain, S.M.; Cesano, F.; Scarano, D.; Edvinsson, T. Resonance Raman and IR spectroscopy of aligned carbon nanotube arrays with extremely narrow diameters prepared with molecular catalysts on steel substrates. *Phys. Chem. Chem. Phys.* **2017**, *19*, 30667–30674. [[CrossRef](#)] [[PubMed](#)]



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