Purification of carbon nanotubes for lithium-sulfur battery application

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Abstract

Carbon nanotubes (CNTs) of high purity are often required in many applications, such as in Lithium-Sulfur batteries (LSBs). To date, no commonly used synthesis techniques can produce pure CNTs, thus purification is essential. Acid-based purification is the most commonly used post-synthesis purification techniques. This research aims to compare the ability of two acids: HNO3 and HCl to remove impurities. The quality of the purification was assessed through LSB battery characterisation and Transmission Electron Microscopy (TEM) imaging. The study found that batteries prepared using the HCl washed CNTs performed slightly better than those prepared with HNO3 washed CNTs. TEM images also demonstrate that while minimal impurities remained on both CNT samples, more side wall defects were observed on HNO3 washed CNTs than the HCl washed CNTs. From these observations, it is concluded that HCl is more suitable to purify CNTs for this application.

Keywords: Carbon nanotubes (CNTs), purification, oxidation, morphology characterization, Lithium-Sulfur batteries (LSBs)

1. Introduction

Nowadays, Lithium-sulfur batteries (LSBs) are starting to gain popularity as they possess higher energy density and theoretical capacity than the commonly found lithium ion batteries. Operation of a LSB is governed by a conversion reaction in the sulfur cathode and metal plating and stripping on the lithium anode (Borchardt, Oschatz, & Kaskel, 2016; Seh, Sun, Zhang, & Cui, 2016; Bruce, Freunberger, Hardwick, & Tarascon, 2012; Yang, Zheng, & Cui, 2013). The absence of topotactic reaction in LSBs provide high theoretical specific capacities for both electrodes, 3860 and 1673 mA h g^{-1} for lithium anode and sulfur cathode respectively. Along with an average cell voltage of 2.15 V, this increases the theoretical energy density of LSBs to 2500 W h kg^{-1} or 2800 W h L^{-1} (Yang et al., 2013; Adelhelm et al., 2015). Moreover, LSBs are environmentally friendly due to the natural abundance of sulfur, which also contributes to the low cost of these batteries (Borchardt et al., 2016; Seh et al., 2016).

The lack of commercial applications of LSB indicates that there are still challenges to overcome before the LSB can successfully be commercialized. Sulfur loading is one of the most important issue in LSB, as high sulfur loading is necessary to achieve high energy density in LSBs (Borchardt et al., 2016). However, sulfur utilisation has often been found to greatly decrease with increasing sulfur loading due to partial conversion of sulfur to Li_2S (Ding, Chien, Hor, Liu, & Zong, 2014). Another problem is the need for a conductive and electrochemically inert host material within the cathode to implant the active material into, due to the electronically insulating nature of sulfur and Li_2S (Manthiram, Fu, & Su, 2013), (Evers & Nazar, 2013). To overcome this, carbon is commonly used (Ma et al., 2016), (Borchardt et al., 2016).

Other than the original carbon form, the utilisation of carbon nanotubes (CNTs) as a host material in LSBs is becoming more common. CNTs are the one dimensional structure of elemental carbon in the sp^2 hybridization (P. X. Hou, Liu, & Cheng, 2008) with diameters of nanometre scale and high aspect ratio (Iijima, 1991). The high aspect ratio allows CNTs to configure into interconnected networks that contribute to long-range conductivity in LSBs (Seh et al., 2016). In addition, the specific capacity of LSB with 20 wt% of CNTs added to its cathode was found to increase from 400 mA h g^{-1}_{Sulfur} (without CNTs) to 485 mA h g^{-1}_{Sulfur} (with CNTs) (Han et al., 2003).

Despite having some favourable properties, utilisation of CNTs are still limited. One of the major issues that inhibit the application of CNTs in various areas is the lack of availability of CNTs with high purity, which is essential in application such as in LSBs. The current synthesis processes of CNTs: chemical vapour deposition (CVD), arc discharge and laser ablation are incapable of producing CNTs without additional impurities (P. X. Hou et al., 2008). Metal catalyst is one of the major impurities in as-synthesized CNTs as it is used in all three synthesis processes (Chiang, Brinson, Smalley, Margrave, & Hauge, 2001). Additionally, CNTs produced by these methods also contain carbonaceous impurities (fullerenes, amorphous carbon, carbon nanoparticles).

The post-purification techniques used to remove impurities within the CNTs are divided into three main categories: chemical oxidation, physical-based purification and multi-step purification. Chemical-based purifications can remove most types of impurities (amorphous carbon, polyhedral carbon and metallic impurities). Yet, only low yields can be obtained with a high chance of destroying the CNTs structure. These might limit the application of CNTs in some fields. Conversely, physical-based purifications can purify CNTs without damaging their structures. Yet, these methods are incapable of purifying large

sample amount. Moreover, as-synthesized CNTs must always be mixed with surfactants to disperse them in solution or treated with chemical-based purification before physical-based purifications can be done.

While both methods have their respective advantages and limitations, combining these methods via multi-step purifications is shown to be the most effective method for removal of impurities from CNTs. In addition, multi-step purification allows different purification steps to be combined and tailored to suit the specific requirements of various CNT applications. The distinctive features of each purification category and its variants are summarized in the Appendix.

1.1 Purpose of project

As previously mentioned, impurities contained within the CNTs constitutes a major drawback in the application of CNTs, especially when CNTs of high purity are required. Among the many existing post-synthesis purification techniques available, none can eliminate all impurities from CNTs without any limitation which may affect the LSB performance. The project will focus solely on acid-based purification of CNTs, the most effective and commonly used method in removal of amorphous carbon and metallic impurities within the CNTs. Previous studies of acid-based purification of CNT have mainly used HNO_3 as solvent as it is inexpensive, nontoxic and has mild oxidation ability (P. X. Hou et al., 2008). However, some have argued that HNO_3 is unfavourable for LSBs as it introduces oxygen functional groups into the LSBs which contribute to lower conductivity and undesirable side reactions with sulfur (X. Li et al., 2014). HCl was also tested in this project as an alternative solvent as no oxygen functional group was contained within the acid.

Through TEM imaging, this project aimed to compare and analyse the quality of CNT samples post acid-based purifications by two different acids: HNO_3 and HCl. This project also aimed to analyse the performance of LSBs created using CNT samples purified by different acids and whether oxygen functional group really affect the LSB performance. Additionally, as sulfur loading highly influences the performance of LSBs, the project also aimed to observe the impact given by different percentages of sulfur loading into LSB cathodes towards battery performance.

2. Methodology

2.1 Acid-based purification of CNTs

Acid-based purification of CNTs is the most commonly used method, which is effective in removal of amorphous carbon and metallic impurities within the CNTs. Two acids (HNO_3 and HCl) were tested separately. The purification procedures for both acids are relatively similar, the only differences are the ratio between CNT and acid and the mixing of CNT and HCl mixture at an elevated temperature.

2.1.1 Purification with HNO_3

2 g of CNTs were dissolved in 200 mL of 10 vol% of HNO_3 solution. Once mixed properly, the mixture underwent vacuum filtration on glass fibre paper and was washed with DI water to neutralize the pH. The solid residue was then dried at 100°C in a vacuum oven before being calcinated at 900°C under Argon atmosphere for 4 hours. The calcination step was used to remove any oxygen and remaining moisture contained in the purified CNTs.

2.1.2 Purification with HCl

The procedures were fairly similar to the SWCNTs purification described by Ciobotaru, Damian, and Iovu (2013), however this project used a different temperature to dry the purified CNTs and the additional step of calcination.

100 mg of as-received carbon nanotubes (CNTs) were mixed with 100 ml of 3M HCl solution in a round bottom flask. The mixture was heated at 70°C using an electric heating plate and stirred for 24 hours under stirring rate of 500 rpm. The same vacuum filtration and calcination procedures as the HNO_3 purification were then applied to the mixture.

2.2 Sulfur loading

Two different percentages of sulfur loading (40 wt% and 80 wt%) were compared to observe the impact of low and high sulfur loadings in LSBs. Purified CNT was mixed with elemental sulfur via melt infiltration at 155°C for 24 hours with the sulfur possessing 40 wt% of the total mass. Melt infiltration was used in this paper due to its simplicity, while also providing accurate control of the sulfur loading process (Borchardt et al., 2016). 155°C is the temperature at which sulfur has its lowest viscosity, resulting in a maximized capillary effect (Seh et al., 2016). The same procedures were followed for the 80 wt% sulfur loading.

2.3 Cathode production

The cathodes were made from mixture of 40 mg purified and sulfur loaded CNTs (host and active material), 5 mg super P carbon black (conducting material) and 500 mg of 1% Polyvinylidene fluoride (PVDF) as a binder. A small amount of N-Methyl-2-pyrrolidone (NMP) was also added to improve the consistency of the slurry mixture. A flat surface of black slurry was created on a small aluminium foil sheet which was then dried inside a vacuum oven at

60°C for 24 hours. Once dried, circular shaped cathodes were cut out from the aluminium foil sheet.

2.4 Battery construction and testing

Battery construction was performed inside a glovebox to provide a vacuum condition. The lithium foil anode was inserted into an anode support. Then, electrolyte and porous separators were placed between the anode and the cathode. The electrolyte was prepared prior to battery assembly and included a mixture of 5 mL 1,3-Dioxolane, 5 mL 1,2-Dimethoxyethane and 2.87 g of 1 M Bis(trifluoromethane) sulfonimide lithium salt. The circular cathode was then placed inside the battery, followed by cathode support. A crimping machine was used to help secure all components inside the battery.

The finished batteries were then connected to individual channel of the battery testing machine. LAND Battery Testing System-Data Processing Software was used to observe the performance of the batteries.

3. Results and Discussion

3.1 Morphological Characterization

Transmission electron microscopy was used to study the surface morphology of as-synthesized CNTs (Figure 1) and acid-treated CNTs (Figure 2 and Figure 3). By comparing these images, the surface morphology differences between before and after purification could be clearly defined. The as-received CNTs are highly agglomerated and contain metallic impurities represented by the dark circles inside the walls. Meanwhile, the purified CNTs are observed to be less agglomerated and the dark circles representing impurities are mostly removed.

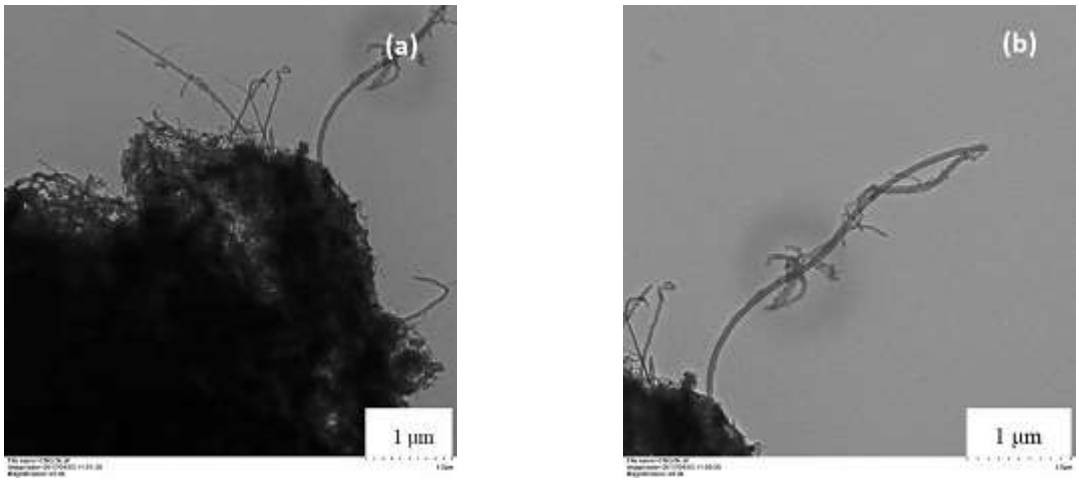

***Figure 1**: TEM images of as-synthesized CNT*

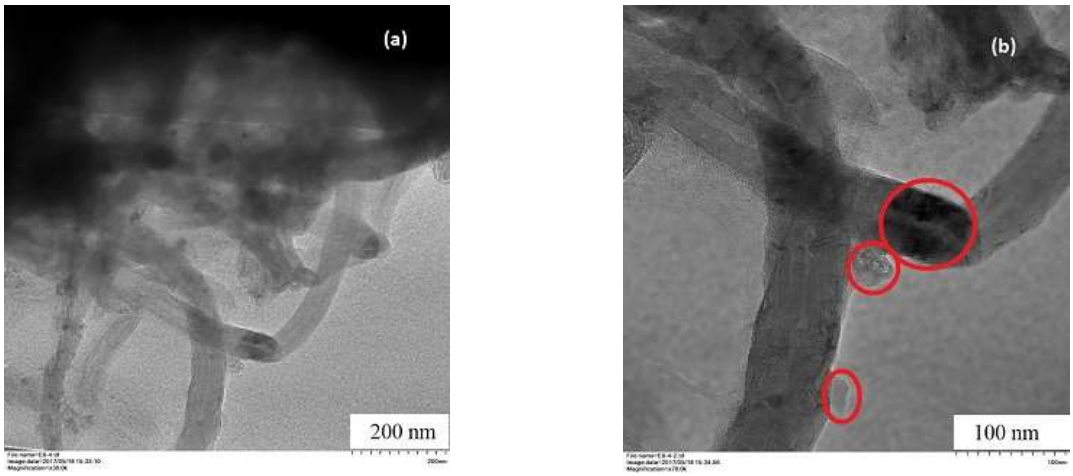

***Figure 2**: TEM images of CNTs treated with 10 vol% HNO3*

In the case of HNO_3 purified CNTs, it can be observed that some metallic impurities remain (area inside the larger red circle in Figure 2b). This finding is consistent with existing literature, indicating that the HNO_3 oxidation only oxidizes the metallic impurities without extracting them (Edwards, Antunes, Botelho, Baldan, & Corat, 2011). This observation also matches the findings by P. X. Hou et al. (2008) and Tsai, Kuo, Chiu, & Wu (2013) who demonstrated that while HNO_3 oxidation is capable of removing both carbonaceous and metallic impurities directly, the effectivity of this method is also dependent on other factors such as the concentration of HNO_3.

The oxidized metallic impurities are shown in Figure 2b by the area inside two smaller red circles, sticking at the outer walls of the CNTs. This is a surface phenomenon that requires physical contact between the metallic impurities and the acid solvent (Edwards et al., 2011). HNO_3 permeates the inner tube via the openings and cuts along the length of the tube, indicating that HNO_3 oxidation has damaged the tube walls (Saito, Matsushige, & Tanaka, 2002; Marshall, Popa-Nita, & Shapter, 2006).

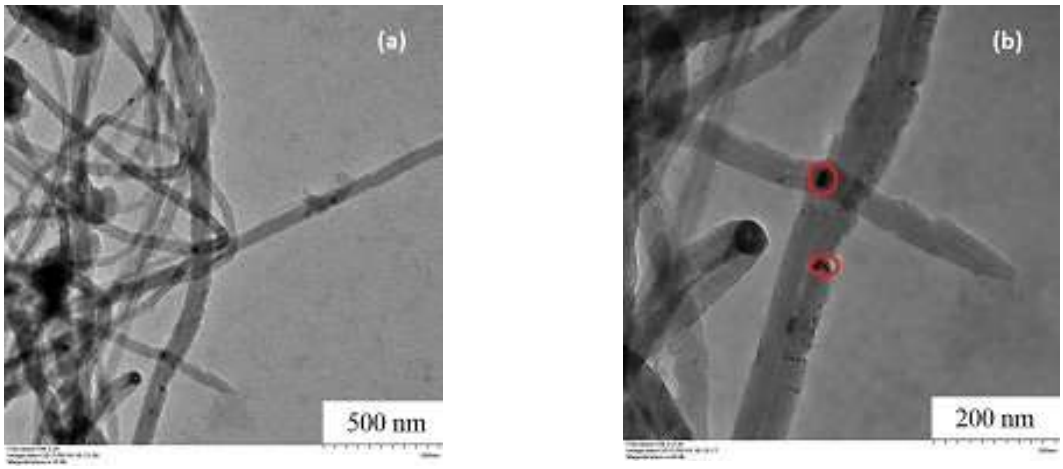

***Figure 3**: TEM images of CNTs treated with HCl 3M*

Figure 3a shows that the CNTs treated by HCl oxidation have slightly less entanglement compared to those treated with HNO_3. The outer wall of CNTs treated by HCl oxidation is also completely free from any oxidized metallic particles. Instead, the metallic particles seem to be divided into smaller fractions that attach to the inner walls (Figure 3b). Again, this aligns with the findings of Edwards et al. (2011), which suggested that the division of metallic particles into smaller fractions were due to dissolution of metallic impurities.

Thus, from the morphology analysis, the HCl treatment can be considered better than HNO_3 treatment as it did not destroy the CNT outer surface. This is vital as CNT surfaces are an important factor for active material loading and thus the performance of the battery.

3.2 Battery Performance

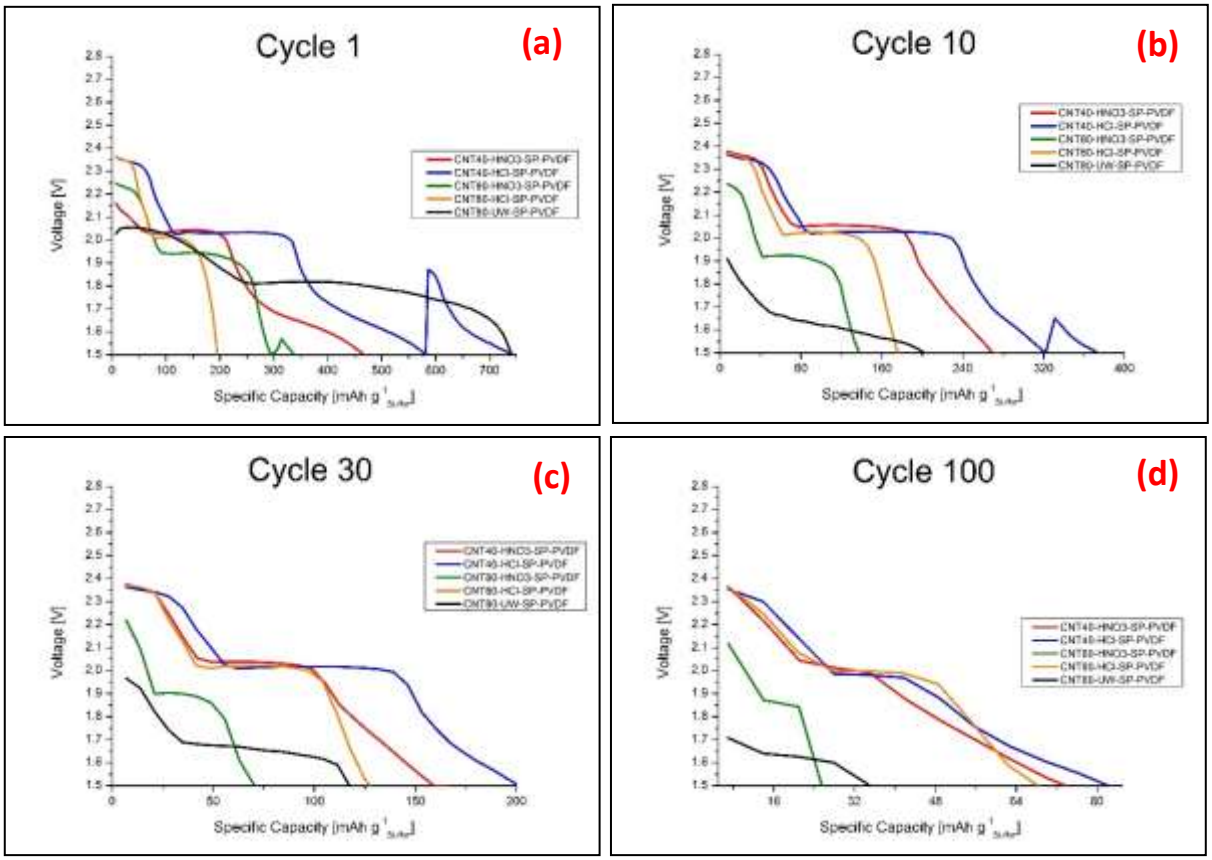

Figure 4*: Discharge voltage profiles of LSBs from different CNT samples at (a) Cycle 1 (b) Cycle 10, (c) Cycle 30, and (d) Cycle 100*

Figure 4 displays the discharge voltage profiles of LSBs made from different CNT samples at different cycles. The operation of LSBs are initiated with discharge, where the following reactions occur simultaneously:

$$\text{At the anode: } Li \rightarrow Li^+ + e^-$$

$$\text{At the cathode: } S_8 + 16Li^+ + 16e^- \rightarrow 8Li_2S$$

Generally, discharge voltage profiles for LSBs show a 2-plateau. The first (upper) plateau corresponds to lithiation of sulfur which forms a series of intermediate, long-chain lithium polysulfide species ($S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4$) that dissolve readily into the

electrolyte (Seh et al., 2016). Meanwhile, the second (lower) plateau represents further lithiation of the dissolved long-chain polysulfides to form short-chain sulfide species (Li_2S_4 → Li_2S_2 → Li_2S), which re-precipitate back into the electrode as solid species (Seh et al., 2016).

From Figure 4, for all samples, the upper plateau can barely be seen, which indicates very rapid reduction of sulfur species at the anode and thus rapid sulfur utilization. Meanwhile, the lower plateau can be clearly observed for most of the samples at different cycles. Both upper and lower plateau for different samples occur between voltage of 2.4V and 2.0V. These voltage values are considered relatively low in comparison to the values cited in the literature, between 2.3 V and 2.1V (Borchardt et al., 2016). While all samples were tested at current density of 0.5C, the LSB made from HCl washed CNT with 40% sulfur loading shows the best performance in comparison to other samples. At the initial cycle (Figure 4a) this sample reaches a discharge capacity of more than 700 mA h g^{-1}_{Sulfur} with a stable decreasing trend at different cycles. In contrast, other samples, such as the LSB made from non-purified CNTs, decrease significantly while also corresponding to lower voltage values.

Another important finding is that the performances of samples loaded with 80% sulfur for both HNO_3 and HCl washed CNTs deteriorate from those of samples loaded with 40% sulfur. This proves the theory by Ding et al. (2014) that sulfur utilisation greatly decreases with increasing sulfur loading due to partial conversion of sulfur to Li_2S. Yet, 40% sulfur loading cannot be deemed as the best sulfur loading value, as the highest discharge capacity provided by this sulfur loading only reaches around 700 mA h $g^{-1}_{Sulfur,}$ while the theoretical optimum discharge capacity of LSBs from literature can reach above 1600 mA h g^{-1}_{Sulfur} (Seh et al., 2016).

4. Conclusions

The study was completed to determine a suitable acid-based purification for CNT for LSB application by testing the quality of purification by two different acids: HNO_3 and HCl. The morphology characterization showed that HCl oxidation is better for this application as it contributes no damage to the surface of CNTs. Likewise, the analysis on LSBs performances showed that HCl washed CNTs contribute to the best battery performance out of all samples, demonstrated through the highest discharge capacity and longer plateau in each cycle. However, it was found that increasing the percentage of sulfur loading from 40% to 80% deteriorated the battery performance for all samples, due to the ineffective sulfur utilization. Since the sulfur utilization greatly affects the energy density of the LSBs, further work is needed to find the optimum sulfur loading percentage, as 40% sulfur loading only contributed to a discharge capacity of around 700 mA h g^{-1}_{Sulfur}, far lower than the theoretical value of more than 1600 mA h $g^{-1}_{Sulfur.}$

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Appendix: Post-synthesis purification methods for CNTs

Chemical Oxidation		
Type	**Characteristics**	**Oxidants**
Gas Phase Oxidation	• Oxidation of carbonaceous impurities at elevated temperature (225-760°C) under an oxidizing atmosphere (P. X. Hou et al., 2008) • Simple method for removal of carbonaceous impurities, but unsuitable for large graphite particles and metallic impurities (P. X. Hou et al., 2008) • Opens the caps of CNTs with minimal additional sidewall defects and functional groups (P. X. Hou et al., 2008) • Only capable of purifying a very small amount of CNTs each time to ensure homogenous contact between oxidizing gas and CNTs (P. X. Hou et al., 2008)	• Air (Harutyunyan, Pradhan, Chang, Chen, & Eklund, 2002; Park et al., 2001; P.X. Hou, Bai, Yang, Liu, & Cheng, 2002) • Mixture of Cl_2, H_2O and HCl (Zimmerman, Bradley, Huffman, Hauge, & Margrave, 2000) • Mixture of Ar, O_2, and H_2O (I. Chiang et al., 2001; I. W. Chiang et al., 2001; Sen, Rickard, Itkis, & Haddon, 2003) • Mixture of O_2, SF_6 and $C_2H_2F_4$ (Xu, Peng, Hauge, & Smalley, 2005) • H_2S and O_2 (Jeong, Kim, & Hahn, 2001) • Steam (Tobias, Shao, Salzmann, Huh, & Green, 2006)
Liquid Phase Oxidation	• Simultaneously removes both amorphous carbon and metallic impurities by oxidation aided by oxidative ions and acid ions dissolved in acid solution with high yield (P. X. Hou et al., 2008) • Leads to surface modification on CNT sidewalls which improves physical and chemical properties of CNTs (P. X. Hou et al., 2008) • Limitations of this method includes adding functional groups, cutting and opening CNTs, depositing oxidation products on CNT surface and loss of smaller diameter SWCNTs (P. X. Hou et al., 2008)	• HNO_3, regularly used as it is inexpensive and nontoxic with mild oxidation ability that effectively removes impurities without adding secondary impurities (P. X. Hou et al., 2008), (Hu, Zhao, Itkis, & Haddon, 2003) • H_2O_2, another inexpensive and mild oxidant that effectively removes carbonaceous impurities but unable to move metal particles (P. X. Hou et al., 2008). Therefore mixture of H_2O_2 and HCl is often used instead (Wang, Shan, Hauge, Pasquali, & Smalley, 2007) • Mixture of H_2SO_4 and HNO_3 with 3: 1 ratio, capable of producing 98% purity with 40 wt% yield (Y. Li et al., 2004)
Physical-based Purification		
Type	**Characteristics**	
Filtration	• Separation based on variation in size, aspect ratio and solubility of CNTs and impurities, for instance removal of fullerenes by dissolution in organic solvents followed by filtering (P. X. Hou et al., 2008) • Physicochemical interactions of CNTs, amphiphilic molecules and filter membrane are the sole driving force for this technique, thus creates no damage on the CNTs (P. X. Hou et al., 2008) • As filter membrane often blocked by larger CNT and impurity particles, surfactants are generally used to prevent agglomeration of CNT suspension followed by ultrasonication to prevent blocking on the filter membrane (P. X. Hou et al., 2008)	
Centrifugation	• In general, working principle of this technique is based on the different settling rates of particles of different masses in response to gravity (Hu et al., 2005), (Yu et al., 2006), (Chun, Fagan, Hobbie, & Bauer, 2008) • Purification by centrifugation can only be done after the CNTs have been treated with nitric acid, thus functional groups are introduced on the CNT surface (Hu et al., 2005), (Yu et al., 2006)	

Solubilization with Functional Groups	• CNTs are purified by introducing functional groups onto the surface to solubilize the CNTs. The soluble CNTs are then subjected to other purification techniques, such as filtration or chromatography (P. X. Hou et al., 2008) • This method is beneficial as it preserves the surface electronic structure of CNTs (Klumpp, Kostarelos, Prato, & Bianco, 2006) and has non-destructive nature. However, this method only yields a small amount of product and incapable of cleaning CNTs with large amount of impurities (P. X. Hou et al., 2008)
High Temperature Annealing	• Capable of removing metal impurities that unable to be removed by acid-based purification, especially if the metallic impurities exist in the hollow core or at the tips of CNTs (Andrews, Jacques, Qian, & Dickey, 2001), (Kim et al., 2004) • The method also capable of altering disordered CNT structures into straight, crystalline layers (Kim, Hayashi, Osawa, Dresselhaus, & Endo, 2003) and increases thermal stability, mechanical strength and electronic transport property (P. X. Hou et al., 2008) • Since this method is incapable of removing carbonaceous impurities, this method is best applied to remove residual metallic impurities from CNTs purified by other methods (P. X. Hou et al., 2008)
Other Physical-based Purifications	• There are other physical-based purification techniques such as chromatography, field-flow fractionation (FFF) and electrophoresis that are capable of separating CNTS based on differences in their length or conductivity. These methods are particularly suitable for CNT application in nano or micro-electric devices (Huang, McLean, & Zheng, 2005; Doorn et al., 2002; Chun et al., 2008)
Multi-step Purification	
Type	**Characteristics**
HIDE-assisted	During hydrothermally initiated dynamic extraction (HIDE) assisted multi-step purification, the network between CNTs, amorphous carbons and metal particles are broken by water molecules. The water molecules also hit graphitic layers covering the metal particles which result in removal of most graphitic nanoparticles and carbon nanospheres (CNSs) from the CNTs. This step is followed by filtration and drying, Soxhlet extraction and chemical oxidations. Yet, even though high-purity CNTs can be achieved from this method, the yield is very small (P. X. Hou et al., 2008)
Microfiltration and Oxidation	As-synthesized CNTs are purified with microfiltration followed by oxidation in heated air to remove CNSs on the CNT walls. The metal impurities are then removed by immersing the CNTs in concentrated HCL at room temperature, resulting final purity higher than 90% (P. X. Hou et al., 2008)
Sonication and Oxidation	Sonication is considered the most effective in removal of amorphous impurities. This method enables interaction between CNTs and solvent which leads to solubilization of CNTs (Nepal, Kim, & Geckeler, 2005). This step is then followed by liquid-based oxidation with HCl as oxidating solvent (P. X. Hou et al., 2001). Similarly to microfiltration and oxidation, this method also capable of producing very high purity CNTs but only in small amount (P. X. Hou et al., 2008)