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Chemical Methods For Purification Of Carbon Nanotubes-A Review

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Abstract

The discovery of carbon nanotubes (CNTs) has stimulated intensive research to characterize their structure and to determine their properties. The unique physical, chemical, mechanical, electrical and electronic properties of CNTs make them candidate material for service in electronic devices, energy storage systems and structural composites, for example. Considerable efforts have been directed for the synthesis, characterization and functionalization of the CNTs. Nevertheless, the CNTs sample obtained by different techniques has the disadvantage of containing non-CNT impurities, such as graphitic particles, fullerenes, residual catalyst particles and amorphous carbon. These impurities will interfere with most of the desired properties of the CNTs. Also in the fundamental research, it is preferred to obtain homogeneous CNTs as pure as possible. Therefore, purification is an essential issue to be addressed. Considerable progress in the purification of CNTs has been made and a number of purification methods including chemical oxidation, physical separation, and combinations of chemical and physical techniques have been developed for obtaining CNTs with desired purity. This review highlights the past and recent developments in the purification of CNTs with focus on the principles, advantages and limitations of chemical oxidation processes aiming to provide guidance to stimulate innovative thoughts on the purification of CNTs.

KEYWORDS: Carbon nanotubes; Purification Methods; Chemical Oxidation.

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1. INTRODUCTION

Carbon nanotubes with excellent physical, chemical, mechanical, electrical, electronic and structural properties find wide promising applications in nanoelectronics, field emission displays, nanoscale sensors, nanostructural composites, catalyst, catalyst support, bio-materials, energy storage media and so on (Thess et al.1996; Ebbesen & Ajayan 1992; Endo et al. 1993). Considerable efforts have been directed for the synthesis, characterization and functionalization of the CNTs. Nowadays, CNTs can be produced by three dominant techniques: chemical vapor deposition (CVD), arc discharge and laser ablation (Iijima 1991; Karthikeyan et al. 2009) Arc discharge and laser ablation are modified physical vapor deposition techniques and involve deposition of hot gaseous carbon atoms generated from the evaporation of solid carbon. However, equipment requirement and the large amount of energy consumed by these methods make them less advantageous. Both laser ablation and arc discharge techniques are limited in the volume of sample they can produce from the carbon source. Chemical vapor deposition is achieved by putting carbon source in gas phase and using an energy source such as plasma or resistively heated coil, to transfer energy to a gaseous carbon precursor molecule. Commonly used carbon sources are petroleum products like methane, ethane, acetylene, etc. The energy source is used to crack the molecule into reactive atomic carbon. The actual mechanism of CNTs formation is still under discussion, but it is suggested that metal catalyst in the substrate dissolves carbon and the carbon diffuse on the particle surface or through the particle bulk or by both process and on saturation precipitated out, where it forms nanotubes. The as grown CNTs contain lot of side products as impurity. The main impurities are graphite sheets (wrapped up), particles and graphitic polyhedrons, amorphous carbon, small fullerenes, substrate materials and metal catalysts. The metal catalyst particles remain at the base of the nanotubes or on its tip or it is incorporated within the Nanotubes (Itkis et al. 2005; Kolodiazhnyi & Pumera 2008). There is no accepted scientific definition for the purity of carbon nanotubes as it can be different from different points of view, such as CNTs content, structural integrity, homogeneity. To evaluate the purity of CNTs, rapid, convenient and unambiguous characterization methods are required. The purity

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assessment and characterization of CNTs are mainly evaluated by scanning electron microscopy (SEM), transmission electron microscopy (TEM)), thermogravimetric analysis (TGA), Raman spectroscopy, XRD and ultraviolet- visible-near infrared (UV–vis-NIR) spectroscopy. As no one assessment technique mentioned above can give a precise and comprehensive quantification of CNTs, a combination of different assessment techniques may be a good choice to give a full understanding of CNTs. Most of the advanced technological applications of CNTs are depends on the purity of CNTs material. As-grown material contain variety of impurities that lead to an impediment to more detailed characterization of the properties of the CNTs and their future applications in industries. Thus attention has to be paid to the issues of purification. The basic principle of the purification methods takes the advantage of difference in aspect ratio, oxidation rate between CNTs and carbonaceous impurities, solubility of CNTs, size of CNTs etc. Purification methods of CNTs can be categorized into two main group's namely chemical and physical methods. The physical method separates CNTs from impurities based on the differences in their physical size, aspect ratio, gravity and magnetic properties etc. In general, the physical method is used to remove graphitic sheets, carbon nanospheres (CNSs), aggregates or separate CNTs with different diameter/length ratios. These processes are relatively mild and do not cause severe damages to the tubes, but they are normally more complex and less effective (Salernitano et al. 2007). The chemical methods separate the product from the impurities mainly based on the fact that carbonaceous impurities are oxidized at a faster rate than CNTs and the dissolution of metallic impurities by acids. Chemical oxidation normally introduces unavoidable defects on the surface of tubes and the pentagonal structure at the tube ends, causing remarkable damages to the structure and morphology of the CNTs. This review highlights the past and recent developments of chemical purification methods and purity assessments of CNTs. The primary goal of this paper is to provide the chemical community with a realistic evaluation of chemical purification methods.

2. PURIFICATION METHODS

2.1 Chemical Oxidation

The carbonaceous impurities co-existing with as-synthesized CNTs are mainly amorphous carbon and Carbon nanoparticles. Compared with CNTs these impurities are easily oxidized due to the presence of more dangling bonds and structural defects. The high oxidative activity of carbon nanoparticles can be attributed to their large curvature and pentagonal carbon rings (Chang & Bard 1991; Colbert et al. 1994). Therefore, chemical oxidative purification is based on the idea of selective oxidation etching, wherein carbonaceous impurities are oxidized at a faster rate than CNTs. The most commonly used chemical purification method involves oxidation of as-synthesized CNTs in both gas phase and liquid phase conditions. The gas phase condition generally refers to oxidation by air, O_2, Cl_2, H_2O, etc. while the liquid phase condition mainly refers to oxidation using a solution of strong acids and electrochemical oxidation. Oxidation often opens the tip of the CNTs. The tips composed of pentagonal rings are less chemically stable than the tube cylinder composed of hexagonal carbon rings. Therefore, during purification, the presence of five-membered rings in the hexagonal array at the tip renders this region susceptible to the oxidative reactions, presumably on the double bonds connecting two pentagons (Delpenx et al. 2005). The disadvantages of this method are that it cuts CNTs, damages surface structure and introduces oxygenated functional groups on CNTs.

2.1.1 Gas phase oxidation

In gas phase oxidative purification, CNTs are purified by oxidizing carbonaceous impurities at a temperature ranging from 225° C to 760° C under an oxidizing atmosphere. The commonly used oxidants for gas phase oxidation include air, a mixture of Cl_2, H_2O and HCl, a mixture of Ar, O_2 and H_2O, a mixture of O_2, SF_6 and $C_2H_2F_4$, a mixture of H_2S and O_2 and steam (Banerjee et al. 2005; Niyogi et al. 2002; Ajayan et al. 1993). High temperature oxidation in air is found to be an extremely simple and successful strategy for purifying arc discharge derived MWNTs, which are metal free and have fewer defects on tube walls. Ebbesen et al. (1994) reported a gas phase purification to open and purify MWNTs by oxidizing the as-prepared sample in air at 750 °C for 30 min. However, only a limited amount of pure MWNTs (1–2 wt%) remained after the above purification, which can be ascribed to two reasons. One is uneven exposure of CNTs to air during oxidation, and the other is the limited oxidation selectivity between CNTs and carbonaceous impurities. Therefore, two routes may be helpful to increase the purification yield using this simple air oxidation. One is to ensure that the as-synthesized CNT samples are evenly exposed to air, and the other is to enhance the difference in oxidation resistance between CNTs and carbonaceous particles towards air. The above suggestions have been verified by some researchers. As an example, Park and coworkers (2001) increased the purification yield to app. 35 wt% by rotating the quartz tube in which the sample was placed, in order to evenly expose the CNTs and carbonaceous impurities to air at 760° C for 40 min. To increase the difference in oxidation resistance between MWNTs and carbon impurities, the difference in oxidation rates of graphite and intercalated graphite was taken into account (Chen et al. 1996 ; Hou et al. 2002 ; Ikazaki et al. 1994). Carbonaceous impurities have higher structural defect densities than CNTs and are therefore more ready to act as reaction sites for intercalated atoms. Thus the oxidation resistance difference between CNTs and carbonaceous impurities can be increased. As an example, Chen et al. (1996) reported a combined purification process consisting of bromination and subsequent selective oxidation with oxygen at 530°C for 3 days. It is obvious that oxidation of the brominated sample occurs more readily than that without bromination. TEM studies showed that CNTs with both ends open were enriched in the purified sample, and the yield obtained by the above process varied from 10 to 20 wt% with respect to the weight of the original carbon sample. Furthermore, they found that the yield depended crucially on the flow rate of oxidant, the amount of initial sample, the manner of packing of the carbon, and the quality of the cathodic soot.

Although MWNTs can be purified by a variety of gas phase oxidation, attempts to use similar procedures for SWNTs result in nanotubes etching away. For example, using the bromine and oxygen system, the yield was app. 3 wt% for SWNT purification, which implies that a large fraction of SWNTs is consumed in the process. This large difference between MWNTs and SWNTs results from two factors. One is the larger amount of curvature experienced by the graphene sheet of SWNTs and the other is metal impurities catalyzing the low-temperature oxidation of carbon. There may, therefore, be two ways to increase the purification yield of SWNTs using gas phase oxidation. One is to select oxidants that can selectively oxidize carbonaceous impurities by a unique selective carbon surface chemistry while leaving SWNTs intact. The other is to remove metal particles before gas phase oxidation. Some positive results have been obtained following the above suggestions. Zimmerman et al. (2000) reported suitable conditions allowing for the removal of amorphous or spherical carbon particles, with or without metal catalyst inside, while simultaneously protecting SWNTs. The purification incorporates a chlorine, water and hydrogen chloride gas mixture to remove the impurities. A SWNT yield of app. 15 wt% and a purity of app. 90% indicate that the carbonaceous impurities are preferentially removed. Based on their experimental observation, hydrogen chloride was required for selective removal of the unwanted carbon. They proposed a mechanism for the purification. Chlorine gas mixture interacted with the nanotubes cap and formed a hydroxy-chloride-functionalized nanotubes cap. Hydrogen chloride in the gas phase purification mixture protected the caps that are more reactive, by preventing hydroxyl groups from deprotonating. The disadvantage of this method is that only small quantities (app. 5 mg) of SWNTs were purified each time. Furthermore, the reagents and produced gases are toxic and explosive, which limits its practical use.

At the same time, some other oxidants that can selectively oxidize carbonaceous impurities were also reported. For example, hydrogen sulfide was reported to play a role in enhancing the removal of carbon particles as well as controlling the oxidation rate of carbon. A purity of app. 95% SWNTs with a yield of 20–50 wt% depending on the purity of raw material was reported. In addition, steam at 1 atm pressure, local microwave heating in air, air oxidation and acid washing followed by hydrogen treatment were also reported to work well to improve the purification yield (Harutyunyan et al. 2002).

Chiang et al. (2001 a, b) clearly elucidated the role of metals in oxidizing carbons and the need for their prior removal. They found that metal particles catalyze the oxidation of carbons indiscriminately, destroying SWNTs in the presence of oxygen and other oxidizing gases. Encapsulated metal particles could be exposed using wet Ar/O_2 (or wet air) oxidation at 225 °C for 18 h. This exposure was attributed to the expansion of the particles because oxidation products have a much lower density (the densities of Fe and $Fe_2O_3$are 7.86 and 5.18 g/cm^3, respectively). Such significant expansion broke the carbon shells and the particles were exposed as a result. Based on the above results, they proposed a multi-stage procedure for purifying SWNTs synthesized by the HiPCO process. Their method begins with cracking of the carbonaceous shells encapsulating metal particles using wet oxygen (20% O_2 in argon passed through a water-filled bubbler) at 225 °C, followed by stirring in concentrated hydrochloric acid (HCl) to dissolve the iron particles. After filtering and drying, the oxidation and acid extraction cycle was repeated once more at 325 °C, followed by an oxidative baking at 425 °C. Finally, 99.9% pure SWNTs (with respect to metal content) with a yield of app. 30 wt% were obtained. The validity of this method was verified by another group (Sen et al. 2003). However, owing to the complicated purification steps, it is hard to purify SWNTs in a large scale.

Xu et al. (2005) developed a controlled and scalable multi step method to remove metal catalyst and non-nanotube carbons from raw HiPCO SWNTs. Their scalable multi-step purification included two processes: oxidation and deactivation of metal oxides. In the oxidation, metal catalysts coated by non nanotube carbon were oxidized into oxides by O_2 and exposed by using a multi-step temperature increase program. In the deactivation step, the exposed metal oxides were deactivated by conversion to metal fluorides through reacting with $C_2H_2F_4$, SF_6, or other fluorine-containing gases to avoid the catalytic effect of iron oxide on SWNT oxidation. The Fe content was remarkably decreased from app. 30 to 1 wt% and SWNTs yield of app. 25–48 wt% was achieved. However, the shortcoming of this method is that it is limited to HiPCO SWNTs, in which the dominant impurity is metal catalyst. Furthermore, the toxicity of the reagents used in this method and the resulting gases are undesirable features.

Gas phase oxidation is a simple method for removing carbonaceous impurities and opening the caps of CNTs without vigorously introducing sidewall defects, although it cannot directly get rid of metal catalyst and large graphite particles. Thus it is a good choice to purify arc discharge derived MWNTs, which contains no metal catalyst. For purifying SWNTs or MWNTs (synthesized by other techniques), acid treatment to remove the metal catalyst is always necessary. Another point worth noting is that CNTs (SWNTs in particular) in agglomerates prevent oxidant gas from homogeneously contacting the whole sample. In order to obtain high-purity CNTs, the amount of sample to be purified each time is quite limited (tens to a hundred milligrams). Therefore, methods that can cause the oxidant gas to homogeneously contact CNT samples are required to obtain high-purity CNTs on a large scale. Recently, Tan et al. (2008) mixed raw SWNTs with zirconia beads to enhance air flow uniformity and increase the exposed surface of raw soot during thermal oxidation in air.[38] The purified samples had yield of app. 26 wt% and metal impurity of app. 7%. Although the purity is not very high, the technique suggests a way to purify SWNTs on a large scale using gas phase oxidation. This method can provide pure and opened CNTs without heavily damaging tube walls, which is a good choice for the application of open-ended CNTs as nano-size reaction tubes or chemical reactors (Ugarte et al. 1996; Sloan et al.1999). For achieving purified CNTs on a large scale, gas phase oxidation need to be modified in the following ways: one is to look for a simple approach and non-toxic reagents to remove metal particles encapsulated by carbon layers; the other is to look for a way that can make oxidant gas homogeneously contact the as-prepared CNTs. In addition, the gas phase oxidation can be combined with other techniques, such as filtration or centrifugation to further enhance the purification efficiency.

2.1.2 Liquid phase oxidation

Although the merits of gas phase oxidation are obvious, it has a drawback that metal particles cannot be directly removed, and further acid treatment is needed. In order to overcome this limitation, liquid phase purification that always simultaneously removes both amorphous carbon and metal catalyst was developed. An Oxidizing agent and the mineral acid dissolved in solution can evenly attack the network of raw samples, and therefore selection of oxidant type and precise control of treatment condition can produce high-purity CNTs in a high yield. The commonly used oxidants for liquid phase oxidation include HNO_3, H_2O_2 and $KMnO_4$ or a mixture of H_2O_2 and HCl, or a mixture of H_2SO_4 and HNO_3, or a $KMnO_4$ and NaOH. The shortcomings of this method are that it causes reaction products on the surface of CNTs, adds functional groups, and destroys CNT structures (including cutting and opening CNTs) (Dujardin et al. 1998; Rinzler et al. 1998; Hu et al. 2003).

2.1.2.1 Nitric acid Oxidation

Nitric acid is the most commonly used reagent for CNTs purification. Its mild oxidation ability, can selectively remove amorphous carbon. In addition, it is inexpensive and nontoxic, capable of removing metal catalysts and no secondary impurities are introduced. Dujardin et al. (1998) reported a one-step method using concentric nitric acid to purify SWNTs synthesized by laser ablation. The as-synthesized SWNTs was sonicated in concentrated nitric acid for a few minutes followed by refluxing under magnetic stirring at 120–130 °C for 4 h. The yield reached 30–50 wt% of the raw sample and the metal amount was decreased to app. 1 wt%. Even though the effectiveness of nitric acid treatment on the purification of SWNTs is confirmed, the relationship between purification yield and purity with systematic and quantitative measurements was not reported before Hu et al.'s work (2003). They established systematic and quantitative relationship between yield and purity by using solution phase NIR spectroscopy. It is clear that the purity and the yield of SWNTs with nitric acid treatment depend on the concentration of the nitric acid and the time of reflux. Mohanapriya et al. (2007), Delpeux et al. (2005), and Zhao et al. (2006) have employed acid refluxing treatment for shorter duration (30 min) in concentrated nitric acid and they observed that this could effectively dissolve the metal particles and open the tube tips without causing significant structural damages to the

CNTs. The X-ray diffractograms (XRD) of purified CNTs showed the removal of metallic impurities as a few peaks corresponding to the catalytic impurities diminished after the acid treatment (Leela et al. 2007). Besides that, Zhao and his colleagues (2006) have also observed the shifting of XRD diffraction peak of the purified sample toward a lower angle which suggests an increase in the inter-layer spacing. This feature was mainly due to the oxidative etching of nitric acid on graphitic walls of CNTs as reported by other researchers (Ko et al. 2005; Chen et al. 2004). During the purification, the nitric acid attacks the defective sites and intercalate into the CNTs to unzip the tube walls by further oxidative etching, which in turn resulted in the increase of the tube inter-layer spacing.

Generally, the reactive carbons were removed through the reaction as: $C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$. The removal of most of the catalyst particles in nitric acid reflux treatment with a prolonged duration up to 24 h at high temperature has been studied in several researches (Wang et al. 2006). The metal particles as well as the carbonaceous impurities could be effectively dissolved and removed from CNTs. However, at such harsh conditions, some oxidative damages were induced to the sidewalls of the nanotubes. The intensity of D-band in Raman spectra, which is mainly due to defects and carbonaceous particles in the sample, is useful to give the degree of disorder present in the sample. Acid-treated CNTs showed an obvious increase in intensity of the D-band, which can be attributed to the defects present along the nanotubes surface after the vigorous acid treatment.

2.1.2.2 Hydrofluoric acid Treatment

Catalyst particles used for growing CNTs by CVD are normally supported on oxides such as silica and alumina in order to provide the active catalyst with the desired stability and nanometric dimensions. Silica support can be easily dissolved in hydrofluoric acid (HF) containing etching agents. Engel-Herbert et al. (2007) have demonstrated that the removal of silica from as-grown CNTs sample is almost complete after an exposure of 5% aqueous HF for 5 min. The HF oxidation prolonged to 60 min at 550°C has also resulted in the burning of smaller amorphous carbon. Most of dense CNT bundles seemed to be separated and isolated by this method. Hernadi et al. (1996) and Igarashi et al. (2004) have reported similar results in which HF has successfully removed the zeolite support without damaging the structure of the nanotubes.

2.1.2.3 Sodium hydroxide Treatment

By claiming that the usage of HF may be harmful, Ramesh et al. (2006) sonicated CNTs in concentrated sodium hydroxide (NaOH) instead of using HF solution to remove the silica support. The scanning electron microscopy (SEM) image clearly showed that silica and alumina supports can be removed effectively after the NaOH treatment. A single step method for the simultaneous purification and opening of multi-walled carbon nanotubes is developed based on the reaction between NaOH and carbon materials Raymundo-Pinero et al. 2005. The redox reactions between carbon and NaOH proceed through the high reactive sites of the material. As a result, NaOH reacts only with the disordered carbon impurities and with the defected parts of the carbon nanotubes, i.e., essentially the tips, while the continuous graphitic layers of the nanotubes walls are not damaged. This is due to the inability of metallic sodium to intercalate into well-organized materials, and it can only proceed to highly disordered carbonaceous impurities (Joncourt et al. 1996). Therefore, in addition to the opening of tubes, NaOH treatment removed the catalytic support, amorphous carbon, and the catalyst metal particles. The mild conditions have removed the metal impurities without damaging the sidewalls.

2.1.2.4 Hydrogen peroxide Oxidation

Hydrogen peroxide (H_2O_2) is also a mild, inexpensive and green oxidant, which can attack the carbon surface. It cannot remove metal particles. Therefore, it is usually used together with HCl. HCl is a widespread chemical that can be easily converted into a harmless salt. Therefore, purifying CNTs using H_2O_2 followed by HCl treatment to remove metal particles has also been intensely investigated. Macro-scale purification, including a first refluxing treatment in H_2O_2 solution and then rinsing with HCl, was reported by Zhao et al. (2006). Their experimental results showed that the size of Fe particles has a great influence on the oxidation of amorphous carbon. Wang et al. (2007) combined two known reactions (oxidation of amorphous carbon with H_2O_2 and removal of metal particles with HCl) into a single pot, which simplified the process. The product yield and purity were improved. Typically, carbon coated iron impurities were simply dissolved by reacting with an aqueous mixture of H_2O_2 and HCl at 40–70 °C for 4–8 h. With this treatment, the purification yield was significantly increased to app. 50 wt% and the purity was up to 96 wt%. According to Wang, the effect of this process on the purification can be summarized as follows. First, Fe particles act as a catalyst by Fenton chemistry, producing hydroxyl radicals, a more powerful oxidant than H_2O_2 which effectively removes amorphous carbon (walling 1975). Second, HCl dissolves the iron nanoparticles upon their exposure. The exposed iron releases ferrous ions as a result of dissolution of the Fe particles in the acid solution. The ferrous ions quickly diffuse into the acid solution, thereby eliminating iron and iron hydroxide precipitation and their unwanted catalytic effect

2.1.2.5 Mixed oxidants

In order to obtain better oxidative effect, mixtures of acid solutions or strong oxidants were employed (Porro et al. 2007; Karthikeyan et al. 2010) Salernitano et al. (2007) compared the effectiveness of purification between nitric acid (HNO_3) and mixtures of nitric acid and hydrochloric acid (HNO_3/HCl) at the ratio of 3:1. The X-ray photoelectron spectroscopy (XPS) analysis performed on the purified CNTs showed an increase in C/Fe atomic ratio more than three times after HNO_3 treatment and more than eight times after immersion in HNO_3/HCl mixture, indicating the presence of synergy effect between the mixed acid solutions. They suggested that the treatment with HNO_3 dissolved the metal particles; meanwhile, HCl ensured the removal of the eventual metal oxides. Ziegler et al. (2005) studied the effect of heated and cooled piranha solution (4:1 v/v 96% H_2SO_4/30% H_2O_2) in oxidative cutting of nanotubes in which the readily available damaged sites on the sidewall of CNTs were removed without increasing the sidewall damage. Results showed that at high temperature, piranha is capable of attacking existing damage sites and consuming the oxidized vacancies to create cut nanotubes, resulting in etching of small diameter nanotubes. In contrast, low temperature piranha attacked the existing damage sites on the sidewall without introducing new damage sites and therefore demonstrated minimal carbon loss and the slow etch rate preserved the original diameter distribution of nanotubes. Zhang et al. (2005) carried out the mixed acid treatment by using mixtures of sulfuric acid and nitric acid (H_2SO_4/HNO_3) in the ratio of 4:1 v/v. A great structural modification was observed after the treatment. It was suggested that some amorphous materials were formed from the reaction between mixed acids and CNTs. Evidence of a direct attack of SWNTs was apparent at locations where SWNTs were not protected by amorphous materials. A lot of broken SWNTs were observed, and most of the broken ends apparently remained open. The TEM images showed that the CNTs bundle with reduced diameter were embedded into these amorphous-like materials. The results obtained showed that mixed acid treatment is a promising method to cut CNTs into fragments with opened ends.

2.1.2.6 Potassium permanganate Oxidation

As discussed above, HNO_3, H_2O_2, as well as microwave-assisted inorganic acid treatments can effectively remove metal particles, but they are not so effective in removing carbonaceous particles owing to the relative mildness in their oxidation. In order to get rid of carbonaceous impurities, liquid oxidants with stronger oxidation activity were also investigated. These oxidants are predominantly mixture of acids and $KMnO_4$.

Colomer et al. (1999) and Fonseca et al. (1996) have reported the effective reflux oxidation using acidified $KMnO_4$. In order to control the oxidation reaction, Colomer and coworkers applied low temperatures of around 80°C. They reported that when the carbon loss was higher than 60%, no amorphous carbon could be found in the remaining nanotube sample. The transmission electron microscopy (TEM) images of pure nanotubes obtained indicated that all aggregates of amorphous carbon had been removed by the treatment, and thus resulted in tips opening. The active carbons were removed through the chemical reaction as: $3C + 4KMnO_4 + 4H^+ \rightarrow 4MnO_2 + 3CO_2 + 4K^+ + 2H_2O$. Hernadi et al. (2001) verified the above conclusion. They obtained MWNTs with oxygen functional groups which were free from amorphous carbon by $KMnO_4$oxidation. Zhang et al. (2003) investigated the effect of $KMnO_4$ in alkali solution on the purification of SWNTs. $KMnO_4$ in alkali solution is a much more moderate oxidant than in acidic solution. The solution cannot effectively open the tube, while it is strong enough to attack the nanotube walls and generate abundant functional groups. The problem of this process is that additional steps are needed to remove the MnO_2 generated during the oxidation. It is desirable to remove carbonaceous impurities by converting them into soluble or volatile products, and from this point of view, $KMnO_4$ seems to be a less suitable oxidizing agent for purification of as-grown CNTs.

Liquid phase oxidation is a continuous process that can eliminate impurities on a large scale, and it is hoped that it can be widely used for industrial application in the future. This method often leads to surface modification that preferentially takes place on CNTs sidewall, which increases the chemical activity and the solubility of CNTs in most organic and aqueous solvents. This surface modification effect shows great potential for improving their physical and chemical properties for specific applications, example in making mechanically reinforced composites, in use as scanning probe microscopy tips with tailored chemical sensitivity, and in producing nanotube derivatives with altered electronic structures and properties (Tasis et al. 2003; Rao et al. 2001). Furthermore, CNTs can be cut into short fragments decorated with oxygen functional groups under suitable treatment conditions, which greatly increases their dispersibility and facilitates their practical applications. For example, the application of CNTs in the field of emerging biotechnology is based on the premise that short CNTs are dispersible in water (Sun et al. 2002) The main problem of this liquid oxidation strategy is the damage to CNTs, the inability to remove large graphite particles, and the loss of a large amount of SWNTs with small diameter. It is very difficult to obtain purified SWNTs with high-purity and high yield without damage by simply using liquid phase oxidation.

2.1.2.7 Electrochemical oxidation

As with liquid phase oxidation and gas phase oxidation, carbon materials with fewer defects usually show a lower corrosion rate under electrochemical oxidation. Therefore, it is reasonable to deduce that CNTs with fewer defects should show higher electrochemical oxidation resistance than carbon with more defects.

Fang et al. (2004) investigated the electrochemical cyclic voltammetric (CV) oxidation behavior of an arc discharge derived SWNTs sample in KOH solution. Amorphous carbon in the as-grown SWNTs sample was effectively removed by the CV oxidation, as confirmed by analyzing the sp^3/sp^2carbon ratio from C_{1s}XPS spectra and TEM observations. The removal of amorphous carbon led to the exposure of metal nanoparticles, hence facilitating the elimination of the metal impurities by subsequent HCl washing. The redox peaks from the electrochemical redox reactions of Fe and Ni impurities can be considered as an indication of the extent of removal of the amorphous carbon, and the optimum electrochemical oxidation time for the purification of the as-grown SWNTs sample can be determined in real time during the CV oxidation treatment.

The above electrochemical oxidation was performed in KOH solution, which needs further acid treatment to remove metal particles. This makes the purification complex. If the solution is acidic, the post-treatment should be omitted, which makes the purification easier. Ye et al. (2006) verified this. They reported an ultra-fast and complete opening and purification of MWNTs through electrochemical oxidation in acid solution. The vertically aligned MWNT (with her ringbone structure) arrays investigated were grown on a carbon micro-fiber network through DC plasma-enhanced CVD. Electrochemical oxidation for tip opening and purification of MWNT arrays was performed in an aqueous solution of 57% H_2SO_4 at room temperature. SEM and TEM images before and after purification indicated that the CNTs tip were opened, and entrapped metals were removed during the electrochemical oxidation. The results of inductively coupled plasma-mass spectrometry indicated that 98.8% of the Ni was removed after the electrochemical oxidation in acid. The authors also investigated a series of electrolyte solutions for electrochemical opening of CNTs tip at room temperature. They concluded that if electrochemical oxidation was performed in neutral or basic aqueous solutions, no significant tip opening was observed. If aqueous solutions of common strong or medium strength acids (5% H_2SO_4, 5% HNO_3, or 25% HNO_3+ 25% H_2SO_4, 5% $H_3PO_4$and 5% CH_3COOH) were used, not only can the amorphous carbon be readily etched but also the metal catalyst can be dissolved.

Superior to the gas phase oxidation and other wet oxidation, the optimum time and degree of electrochemical oxidation for CNTs purification can be easily determined. This method can get rid of impurities to some extent, particularly for selectively opening and purifying vertically aligned CNTs arrays. The desired vertical orientation can be maintained and facilitates the use of CNTs arrays as fuel cell electrodes, sensor platforms, nanoreactors, field emitter components, and other applications. However, little polyhedral carbon, graphite particles, and metal particles enwrapped by carbon layers with fewer defects can be removed by the CV oxidation. Moreover, the purity of the obtained sample greatly depends on the starting materials, and the amount of sample purified for each batch is too small to make the method practical.

The purification of CNTs through the physical methods has not attracted much attention compared to that of chemical methods due to its mild condition which normally leads to ineffective purification. However, the advantages of these physical separations are the impurities such as nanocapsules, and amorphous carbon can be removed simultaneously, and the CNTs are not chemically modified. Purification of CNTs can be carried out by combining the chemical treatment and physical separation in a multi-step procedure in order to effectively remove the amorphous carbon, metal particles, and multi-shell carbon nanocapsules. Multi-step purification is necessary particularly when a single treatment is not sufficient to simultaneously remove all the impurities that are present in the CNTs. It was found that these procedures are efficient and appropriate to obtain high purity CNTs with minimal wall damage.

3. CONCLUSION

Chemical-based purification can effectively remove amorphous carbon, polyhedral carbon and metal impurities at the expense of losing a considerable amount of CNTs or destroying CNT structures. Gas phase purification is characterized by opening the caps of CNTs without greatly increasing sidewall defects or functional groups. Liquid phase oxidation introduces functional groups and defects preferentially on CNTs side wall and may cut CNTs into shorter ones with different lengths. The electrochemical oxidation is suitable for purifying CNT arrays without destroying their alignment. These features allow chemical purification adopted by researchers to fulfill different requirements. The most serious problem of this technique is that the structure of CNTs may be destroyed by the reactants, and hence limits the applications of CNTs in some fields, for example, electronic devices. However, with proper control of the reaction conditions, purification of CNTs through the removal of metal catalyst particles may result in higher purity as well as the tips opening.

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