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High Yield Purification of Carbon Nanotubes with H_2S-O_2 Mixture

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Abatract−A high yield purification method was developed for multi- and single-walled carbon nanotubes, combining both the gas-phase purification using H_2S and O_2 mixture to remove impurity carbon particles and the acid treatment to remove metal particles. For the purification of MWNTs, the purification yield was about 54%, much higher than the yield previously reported. For the SWNTs, the combined liquid-gas purification process resulted in a high purity of >95% and a high yield of 20-50%, depending on the quality of raw material. Hydrogen sulfide played a role of enhancing the removal of carbon particles as well as suppressing the oxidation of carbon nanotubes. Overall, the purification method developed in this work is simple and quite effective for removing unwanted carbon and metal particles out of MWNTs and SWNTs.

Key words: Carbon Nanotubes, High Yield Purification, H_2S-O_2

INTRODUCTION

Carbon nanotubes have attracted much attention because of their fascinating electronic and mechanical properties, such as high modulus [Yakobson et al., 1996; Salveta et al., 1999] and structural diversity [Mintmire et al., 1992; Hamada et al., 1992], effective field emission characteristics [Collins et al., 1997; Fan et al., 1999], and capability for hydrogen storage [Dillon et al., 1997; Nutzenadel et al., 1999]. There are two kinds of carbon nanotubes: multi-walled and single-walled. Conventional dc arc discharge method is generally used to produce multi-wall carbon nanotubes (MWNTs) in large quantity [Ebbessen and Ajayan, 1992; Journet et al., 1997]. However, this method also produces a large amount of impurity particles such as graphite and amorphous carbon particles, which are always mingled with carbon nanotubes [Ando et al., 1993; Colbert et al., 1994]. Single-wall carbon nanotubes (SWNTs) are produced by several methods, such as arc-discharge method in the presence of a transition metal catalyst, pulsed laser vaporization, chemical vapor deposition, and catalyst-assisted decomposition. However, the SWNTs produced by these methods also contain a large amount of impurities such as graphite, amorphous carbon and catalytic metal particles. As these impurities cause a serious impediment for their detailed characterization and applications, they have to be removed for further physical and chemical processing.

There are several ways of purification of MWNTs such as filtration, chromatography, centrifugation, thermal oxidation in air, and infrared radiation heating method [Ebbesen, 1997; Yoshinori et al., 1998; Park et al., 2001]. It is known that MWNTs are purified to some extent by using the methods mentioned above, but still contain impurities and thus the yield is very low in most cases (<20%). Furthermore, these methods have some difficulty in controlling the oxidation rates between carbon nanotubes and impurity particles. The purification methods for the MWNTs proved to be inapplicable to the SWNTs because compared to the MWNTs, the SWNTs have larger curvatures and higher chemical reactivity, resulting in SWNTs being destroyed prior to impurity particles [Shelimov et al., 1998].

Several methods for the purification of SWNTs, such as ultracentrifugation, microfiltration, cross-flow filtration, and oxidizing-acid reflux method [Shelimov et al., 1998; Jeong et al., 2001] have been studied. However, it is known that sonicating nanotubes for a long time and at high frequency can cause damage by breaking the nanotubes into smaller pieces. The filtration method also has the disadvantage that it leaves some amorphous carbon particles and multishell nanocapsules from SWNT samples, and is a quite complicated process. Hence, a gas-phase or a combined liquid- and gas-phase purification method needs to be developed [Jeong et al., 2001].

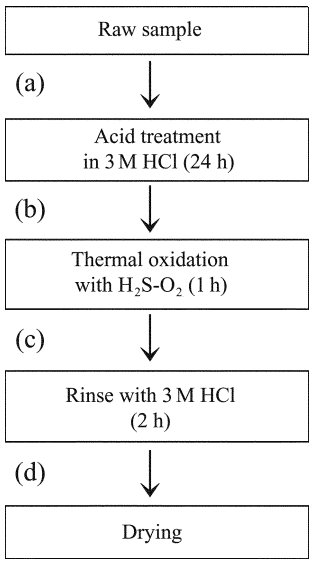

Fig. 1. Process flow of the purification of SWNTs.

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In this work, we present a simple and efficient method for purification of carbon nanotubes: a thermal oxidation using a H_2S-O_2 mixture for MWNTs and a combined liquid- and gas-phase purification for SWNTs. The thermal oxidation using hydrogen sulfide and oxygen gas mixture was used to remove impurity carbon particles, and the liquid treatment using 3 M HCl solution to eliminate catalytic metal particles. After the purification process, the nanotubes were examined by SEM (scanning electron microscopy), EDS (energy dispersive spectroscopy), and Raman spectroscopy.

EXPERIMENTAL

Carbon nanotubes were prepared by a conventional electric arc-discharge method under helium atmosphere using two graphite rods with diameters of 10 mm and 25 mm as an anode and a cathode, respectively. Growth conditions were 400 Torr, 20 V and 100 A of DC current for MWNTs, and 100 Torr, 25 V and 80 A for SWNTs. The SWNTs were grown by inserting 5% of a mixture of Ni, Co and Fe metals (Ni : Co : Fe=1 : 1 : 1) into the small hole in a graphite rod. Approximately 100 mg of raw material was used for all purification experiments as received.

For purification of MWNTs, nanotubes were thermally oxidized to remove impurity carbon particles with O_2, H_2S-O_2 mixture, and/or H_2S/O_2 plasmas at various conditions. One-step oxidation method was adopted to oxidize impurity particles in MWNTs. By contrast, the SWNTs were purified by a multi-step method, combining the liquid-phase treatment using 3 M HCl to eliminate catalytic metal particles and the gas-phase oxidation using the H_2S-O_2 mixture to remove carbon particles.

Fig. 1 shows the purification method for the SWNTs. As a first

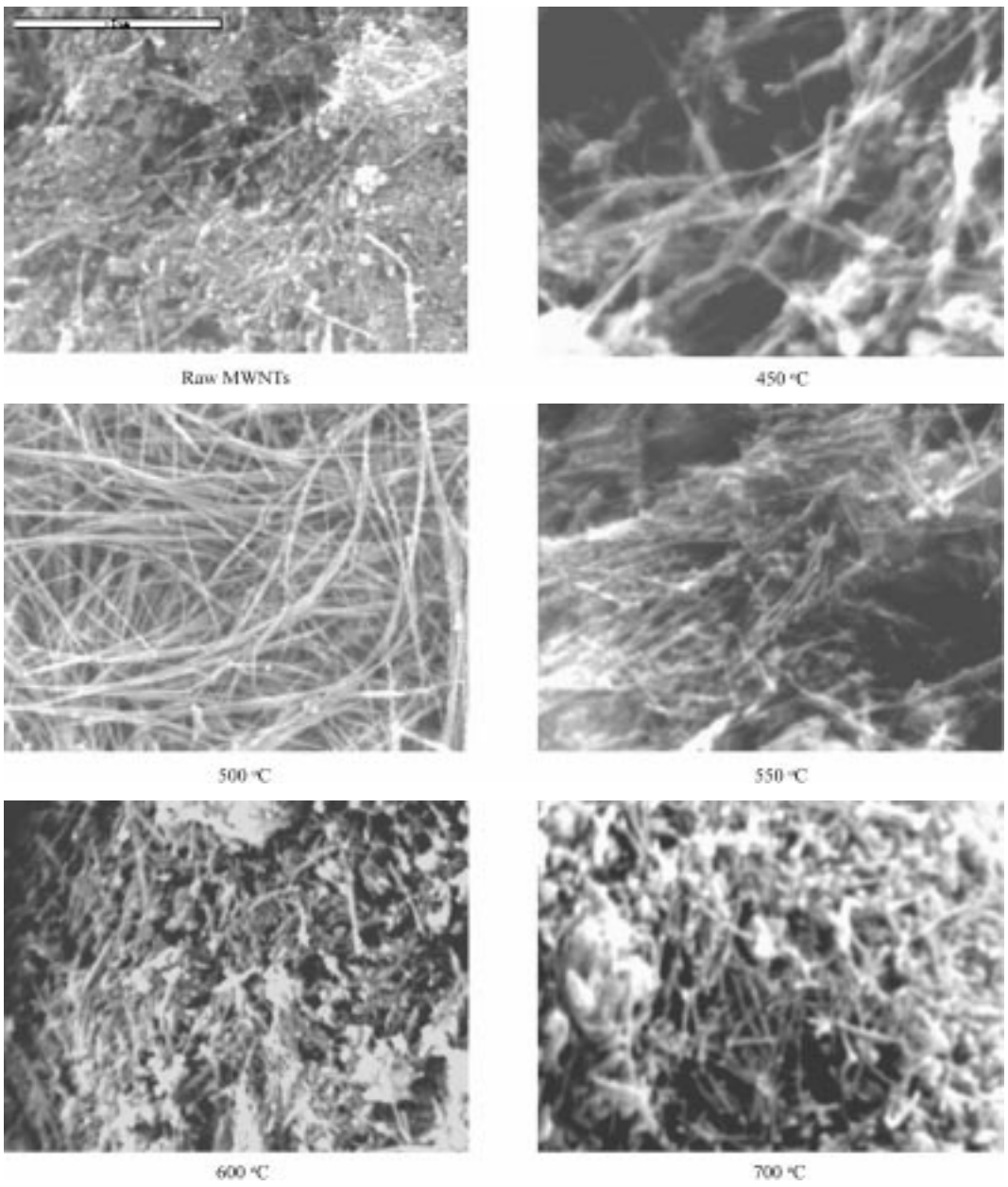

Fig. 2. SEM micrographs of the raw and the MWNTs purified by H_2S-O_2 oxidation at various temperatures for three hours.

step of purification, the raw sample (100 mg) of SWNTs was suspended in 3 M HCl solution at room temperature to remove metals and refluxed for 24 h. The supernatant liquid was then decanted off and the black sediment was resuspended in deionized water. This procedure was performed more than three times, and the sample was dried at 150 °C for 24 h. In order to remove amorphous carbon and nanoparticles, the SWNTs were then oxidized at 500 °C for 1 h by using hydrogen sulfide and oxygen. The oxidized samples were suspended in 3 M HCl solution for 2 h to further remove any metal particles remaining after the oxidation process. The samples were then finally dried at 150 °C for 24 h and weighed for yield data.

RESULTS AND DISCUSSION

1. Purification of Multi-walled Carbon Nanotubes

Fig. 2 shows a typical SEM image taken at the raw sample of MWNTs synthesized by the arc-discharge method (a), and the nanotubes purified by oxidation using the H_2S-O_2 mixture at various temperatures (450-700 °C) for three hours. During these experiments, the flow rates of H_2S and O_2 were kept constant at 9 ml/min and 22 ml/min, respectively. The raw sample seems to show no carbon nanotubes on the surface because the MWNTs were mostly embedded inside the carbonaceous particles. This indicates that there exists a large amount of impurity particles, mostly amorphous carbon. With oxidizing at 450 °C, some of the carbon particles were removed out of the surface. At 500 °C, most of the impurity particles were removed and the yield was about 54%, much higher than the yield previously reported. However, at temperatures higher than 500 °C, some part of carbon nanotubes was also oxidized and showed broken or shorten nanotubes together with soot sitting on the surface. At higher temperatures, the impurity carbon particles are initially burned out, but as the time proceeds, more carbon nanotubes are exposed on the surface and thus have more chance to be attacked by reactive gas species, resulting in oxidation of nanotubes and low yield of purification.

The possible chemical reaction of hydrogen sulfide with amorphous carbon and oxygen is:

$$C(s)+H_2S(g)+O_2(g)\rightarrow COS(g)+H_2O(g),\ \Delta G_r^o=-403\ \text{kJ/mol}.$$

This reaction was confirmed with water vapor condensing at the exit of the reactor. We believe that some of oxygen reacts with amorphous carbon, which results in formation of carbon dioxide or carbon mono-oxide, and the rest of the oxygen reacts with hydrogen sulfide and amorphous carbon, resulting in formation of carbon oxysulfide (COS) and water vapor. Hence, the hydrogen sulfide may play a role of enhancing the removal of carbon particles as well as controlling the oxidation rate of carbon with oxygen.

Fig. 3 shows a comparison of SEM images of MWNTs, purified with pure oxygen (a) and the H_2S and O_2 mixture (b), respectively, at 500 °C for 3 h. Although the pure oxygen purification method seems to be competitive with the H_2S-O_2 method, nanosize carbon particles are still left on the nanotube surface and the yield of the former (20%) is much lower than the latter (54%).

Fig. 4 represents FT-Raman spectra of raw and purified MWNTs at various temperatures. Raman spectra of both raw and purified MWNTs clearly show the peaks centered at 1,583 cm^{-1} (G-line), indicating the formation of well-grown carbon nanotubes. The peaks

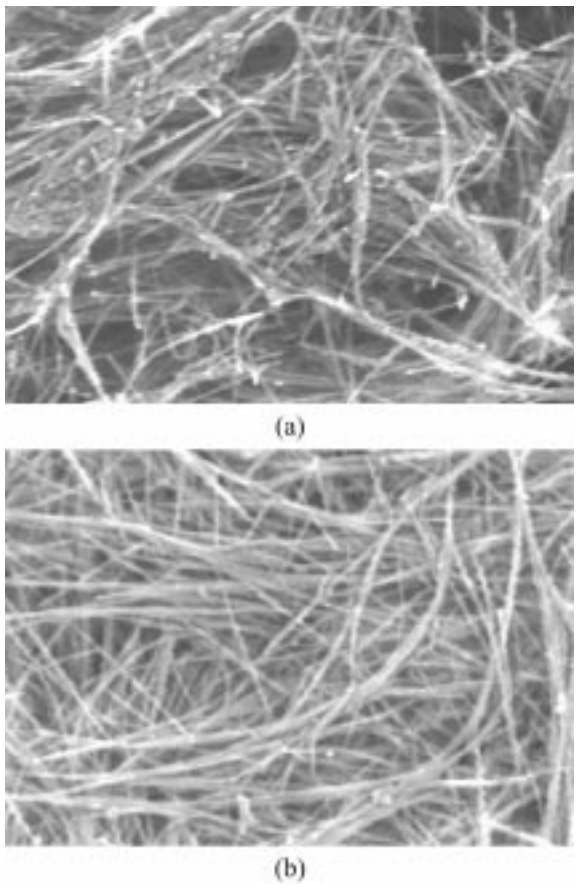

Fig. 3. Comparison of SEM images of the MWNTs, purified with pure oxygen (a) and the H_2S-O_2 mixture (b) at 500 °C for 3 h.

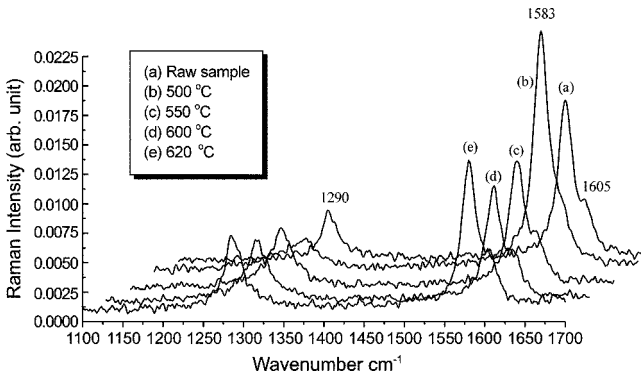

Fig. 4. FT-Raman spectra of the raw and the purified MWNTs at various temperatures.

located at 1,605 cm^{-1} suggest that these carbon nanotubes are multiwalled [Eklund et al., 1995; Park, 2001]. The peaks at 1,290 cm^{-1} (D-line) are attributed to amorphous carbon and defects such as pentagons and heptagons in graphite [Hiura et al., 1993; Li et al., 1997]. Compared to the raw and other samples, the MWNTs purified at 500 °C showed a substantial increase in peak intensity of the G-line, but a decrease in the D-line intensity. This Raman study also indicates that 500 °C is an optimum temperature for the purification of MWNTs with the H_2S and O_2 mixture.

In order to see the feasibility of utilizing a plasma for the purification nanotubes, raw samples were treated in H_2S/O_2 discharge at 500 °C for 1 h, which was an inductively coupled plasma generated by a radio frequency generator (13.56 MHz). Fig. 5 shows the effect of rf source power on the purification of MWNTs in terms of SEM images. Compared to the raw sample (a), the samples were purified to some extent at low power of 30 W (b). By contrast, the samples were over-etched at higher source powers (c and d) and showed a sponge-like structure. This may be attributed to over-oxidation of carbon nanotubes as well as impurity particles with reactive species such as oxygen, hydrogen, and sulfide radicals at higher source power. However, the result at 30 W leaves the possibility that we may have good purification by controlling the reaction time, temperature, and the source power.

2. Purification of Single-walled Carbon Nanotubes

Based on the optimum condition for removing the amorphous car-

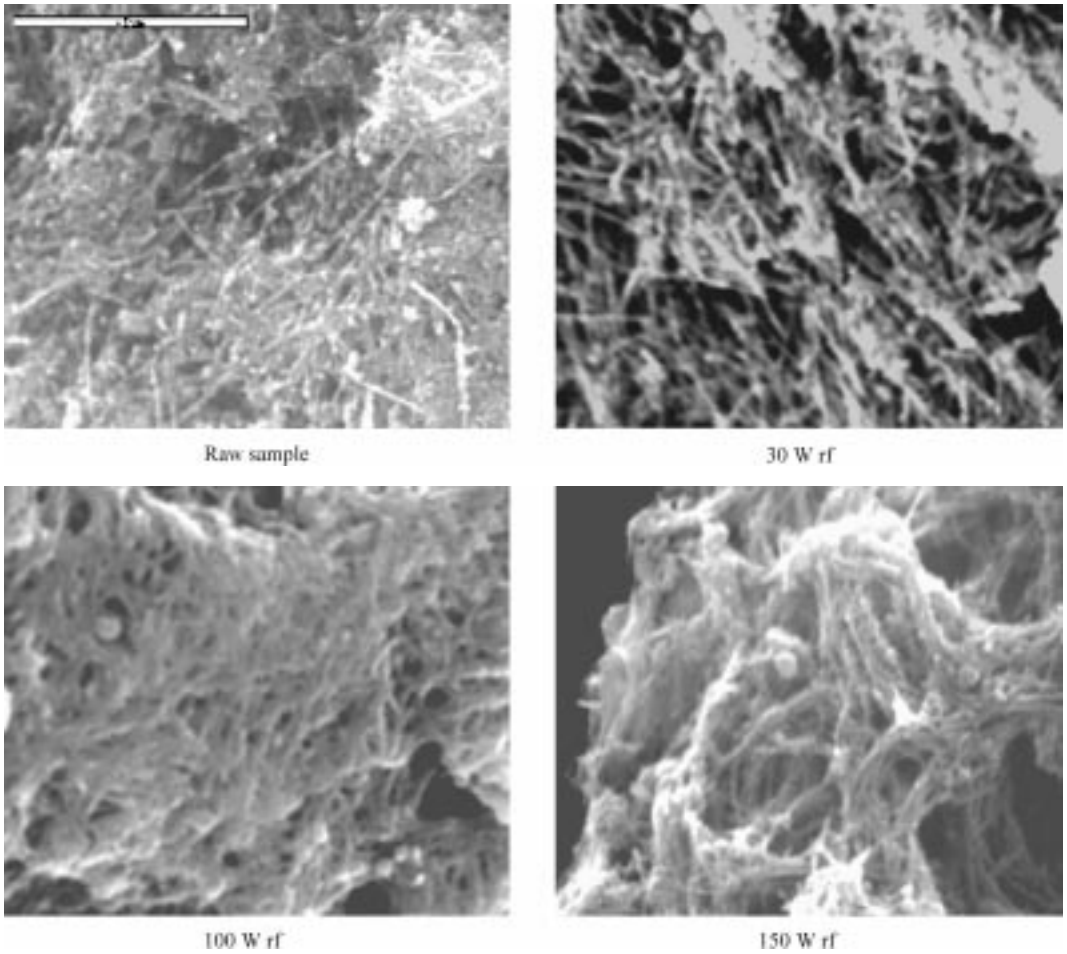

Fig. 5. SEM micrographs of the raw and the purified MWNTs with H_2S/O_2 plasmas at various rf powers.

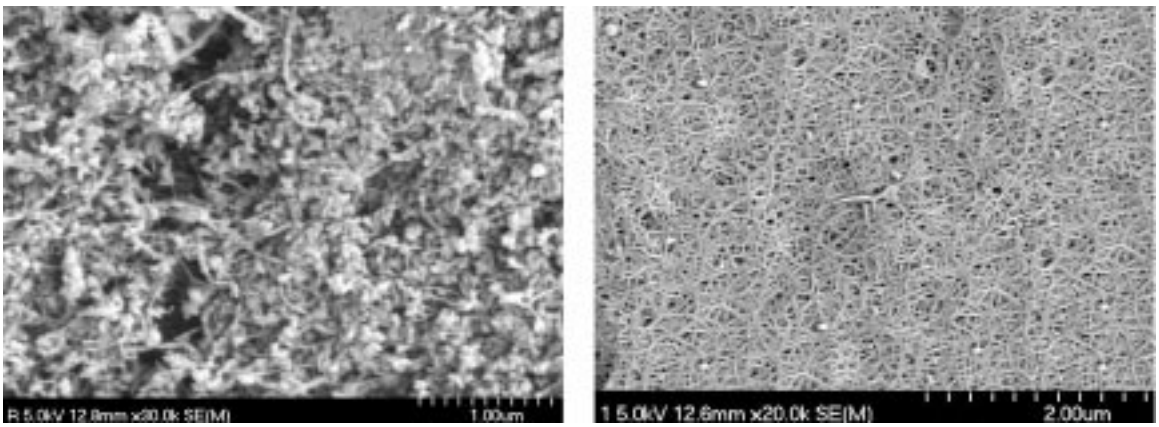

Fig. 6. SEM micrographs of the raw (left) and the purified (right) SWNTs with the combined acid treatment and H_2S-O_2 oxidation.

bon particles of MWNTs, the purification process depicted in Fig. 1 was carried out for the SWNTs. Fig. 6 shows typical micrographs of SEM taken at the raw (left) and the purified (right) SWNT samples. In general, the SWNTs are coexisting with a large amount of amorphous carbon, onionated and metal particles embedded into the amorphous carbon. The amount of SWNTs produced by the arc-discharge method was estimated at less than 30%. After acid treatment and thermal oxidation using H_2S and O_2 at 500 °C for 1 h, high density SWNTs were observed at random orientation with no carbon nanoparticles and amorphous carbon but with a few of metal particles, as shown in Fig. 6 (right). The purification yield obtained varied from 20 to 50%, depending on the purity of the starting raw material. The cleaned SWNTs showed a high purity of >95%, which was defined as the ratio of the area of impurity particles to that of SWNTs. Details in terms of Raman spectroscopy of each step of the purification process are available in our previous work [Jeong et al., 2001], in which the role of H_2S was described as enhancing the removal of carbon particles and suppressing the oxidation of nanotubes.

Compared to purification methods reported previously, the process developed in this work is quite simple and effective to remove unwanted carbon and metal particles out of MWNTs and SWNTs. However, for a better understanding of the mechanism of selective oxidation of carbon particles from nanotubes, a further study is needed in terms of oxidation kinetics of the H_2S-O_2 mixture.

SUMMARY AND CONCLUSIONS

We developed a new purification process of multi- and single-walled carbon nanotubes, combining both the gas-phase purification using H_2S and O_2 mixture to remove impurity carbon particles and the acid treatment to remove metal particles. H_2S played a role of enhancing the removal of carbon particles as well as suppressing the oxidation of nanotubes. For the purification of MWNTs, a one-step process of thermal oxidation using the H_2S-O_2 mixture was suitable, and at 500 °C most of the impurity particles in MWNTs were removed. The purification yield was 54%, much higher than the yield previously reported. However, at temperatures greater than 500 °C, some parts of carbon nanotubes were also oxidized and broken or shortened. For the SWNTs, the combined liquid-gas purification process resulted in a high purity of >95% and a high yield of 20-50%, depending on the quality of raw material. Overall, the purification method developed in this work is simple and quite effective for removing unwanted carbon and metal particles out of MWNTs and SWNTs.

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