A green access to highly pure single-walled carbon nanotubes by taurocholate-assistant dispersion and centrifugation

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Abstract. Raw single-walled carbon nanotubes produced by arc discharge were oxidized in the air to eliminate amorphous carbon, and then dispersed in the aqueous solution of sodium taurocholate supersonically. Thus obtained stable dispersion was subjected to centrifugation, and the metal catalysts and varying carbon impurities were separated with carbon nanotubes. The efficiency of the above procedure was confirmed by scanning electron microscope observation, thermogravimetry, and optical absorption and Raman spectroscopic analyses. The advantage of this procedure lies in easiness, high purity, and no pollution to environment.

1. Introduction
Since discovered by lijima in 1991 [1], carbon nanotubes have been investigated actively and widely. Because of their unique one-dimension structure, high surface area, electrical conductivity, and extremely high strength, single-walled carbon nanotubes (SWNTs) are proposed to have many promising applications in nanoelectronics, nanopores, nanostructural composites, field-emission displays, chemical sensors, etc. [2,3] To realize these potentials and to study their intrinsic properties, high quality SWNTs are required. Unfortunately, the available methods for large-scale production of SWNTs generate significant amounts of carbonaceous impurities, such as amorphous carbon, fullerene, turbostratic graphite, and polyhedral carbon nanoparticles, along with transition metals that were introduced as catalysts in the growth of nanotubes [4,5]. Normally, amorphous carbon is removed by acidic treatment of starting raw material or burning them in air under a relatively high temperature [6,7]. The oxidation of SWNTs has been studied previously [8-13], and strong oxidizing agents such as KMnO₄, HNO₃, and O₃ are applied. These chemicals could damage SWNTs, offer little selectivity to remove metal catalysts, and be environment unfriendly.

In this paper, raw SWNTs prepared by arc discharge are purified by a biological reagent assisted dispersion and then subjecting to centrifugation. The high purity of thus treated SWNTs is checked by scanning electron microscope observation, thermogravimetry, and optical absorption and Raman spectroscopic analyses. In sharp contrast to those purification processes reported previously, a simple and efficient method is developed, in which application of strong acid or strong base and toxic solvents such as THF, DMF are avoided.

2. Experimental
Raw SWNTs are prepared by arc discharge using Tb/Ni powers as catalysts, and FeS as promoter. In a typical experiment, 100 mg raw SWNTs are first oxidized in the air at 400°C for 4 hours to remove amorphous, and the remaining material is then dispersed in an aqueous solution of 1% (wt%) sodium
taurocholate [14,15] by ultrasonic agitation. Thus obtained stable dispersion is subjected to centrifugation for 3 hours at 15000 rpm. The upper suspension is decanted and filtrated with 1µm poly-(tetrafluoroethylene) (PTFE) membrane. After drying for 1 h at 100 °C in a vacuum, the solid sample is heated at 200 °C for 20 min in dry air to remove sodium taurocholate.

Scanning electron microscope (SEM) observation was carried out with a JEOL JSM-6700FT field emission electron microscope (accelerating voltage: 5.0 kV; beam current: 10 nA); Thermogravimetric analysis (TGA) data were recorded with a SII Seiko Instruments EXSTAR 6000 thermogravimetric analyzer; Raman spectra were measured with a Jasco NRS-2100 spectrophotometer using laser excitation at 457.9 nm; The solution-phase optical absorption data were recorded with a Shimadzu UV-3150 spectrophotometer using a quartz cell with a path length of 10 mm.

3. Results and discussion

From figure 1(left), the SEM image of raw SWNTs, it can be observed that some amorphous carbon is on the surface of tube bundles, and SWNTs entangle with carbon and metal catalyst particles. Figure 1(right) shows the SEM image of purified SWNTs, in which high-density SWNTs are observed with few impurities. It is obvious that the purified SWNTs show cleaner surfaces and larger bundles than those observed in figure 1(left).

TGA was also used to check the raw and purified SWNTs to illuminate the result of the procedure for purification of nanotubes. Curves a and b in figure 2 represent typical weight losses of the raw and purified SWNTs, respectively. As curve a shown, amorphous carbon begins to combust at about 350°C and is mostly consumed around 400°C. The weight loss between 435°C-595°C is due to the oxidation of surviving SWNTs. The small loss between 595-773°C is because of the oxidation of carbonaceous
nanoparticles that have higher thermal stability than SWNTs. The prominent weight loss observed for curve b starts at 600°C and ends at 810°C, which could be ascribed to the burning of SWNTs. It is obvious that most of the carbonaceous impurities have been removed. On the other hand, the residual metal oxides after burning of carbonaceous materials decrease from 23% in the raw SWNTs to 3% in the purified ones. Furthermore, the combustion temperature of SWNTs increases from 435-595°C to 600-810°C, which is mainly owning to the removal of metal catalysts. Thus, it is concluded that the purification procedure is efficient to remove both carbonaceous impurities and metal catalysts.

It is suggested that the area ratios of the Raman peaks (G/D) are proportional to the in-plane crystallite size and inversely proportional to the quantity of “unorganized” carbon in graphitic materials [16,17]. Figure 3 shows the Raman spectra of the raw (a) and the purified (b) SWNTs, respectively. The integrated ratio of the Raman peaks (G/D) increase from 21 for the raw SWNTs to 50 for the purified ones. Moreover, it is also noted that the RBM mode of the purified SWNTs has a higher intensity than that of the raw materials. Thus, the purification procedure leads to a dramatic improvement in the purity of SWNTs. It is worth mentioning that the RBM mode has an obvious blue shift for the purified SWNTs in comparison with that of the raw materials. Such shift is most probably due to the increase in bundle’s size, implying that the purification process generates SWNTs with good crystallization. This result is consistent with that observed in figure 1(right).

In the optical spectra of SWNTs by arc-discharge, three characteristic absorption bands are usually observed at approximately 1800, 1000, and 700 nm, respectively, superimposed on a broad background [18]. Figure 4 shows the absorption spectra of the raw and the purified SWNTs, respectively. It is obvious that the characteristic absorptions at 1000 and 700 nm of the purified SWNTs are much stronger than those of raw ones, indicating a large improvement in the purity of SWNTs.

Haddon et al [19,20] proposed a spectroscopic approach to quantitatively evaluate the purity of SWNTs. Even though a 100% pure reference is unavailable and it could not generate absolute purity of SWNTs. However, it could be applied to estimate the efficiency of the present purification procedure. Figure 5 shows the solution-phase NIR absorption spectra of the raw and purified SWNTs, respectively, in the range of 850-1290 nm. From figure 5a, it is estimated that the integrated areas

![Figure 3](image3.png)

![Figure 4](image4.png)

![Figure 5](image5.png)
ratio under the curve after and before baseline subtraction is about 0.241 \( \frac{A(S^{22,F1})}{A(T,R_2)} = 162.66/674.01 \) for the purified SWNTs. In contrast, it is about 0.0411 \( \frac{A(S^{22,R})}{A(T,R)} = 27.2635/665.14 \) for the raw SWNTs. This means that the proposed purification procedure could generate SWNTs with purity about 5.8 times of the raw SWNTs.

4. Conclusion

In summary, we developed a simple and efficient procedure for purification of raw SWNTs, which takes advantage of oxidization at 400°C in dry air, dispersion in an aqueous solution of sodium taurocholate and centrifugation. From the results of SEM, Raman spectra, optical absorption, and TGA analyses, high quality of SWNTs are obtained. In addition, the present purification procedure is environment friendly since it does not involve strong acid, strong base and toxic solvents.

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