

Minimizing Purification-Induced Defects in Single-Walled Carbon Nanotubes Gives Films with Improved Conductivity

Yu Wang¹, Liping Huang¹, Yunqi Liu¹ (✉), Dacheng Wei¹, Hongliang Zhang¹, Hisashi Kajiura² (✉), and Yongming Li²

¹ Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

² Materials Laboratories, Sony Corporation, Okata, Atsugi City, Kanagawa 243-0021, Japan

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ABSTRACT

A method for the non-destructive purification of single-walled carbon nanotubes (SWNTs) using classical coordination chemistry to remove the metal catalyst has been developed. In preliminary tests, the conductivity of films based on the resulting SWNTs was markedly better than that of films prepared from SWNTs purified by treatment with oxidizing acid solutions. The transparent and conducting SWNT films have potential applications in optoelectronic devices.

KEYWORDS

Carbon nanotube film, conductivity, transparency, coordination chemistry

Introduction

Single-walled carbon nanotubes (SWNTs) are under intense investigation owing to their spectacular mechanical and electronic properties [1–3]. Their potential applications range from components in integrated circuits, logic gates, flat panel displays to nanoscale motors [4–6]. Nevertheless, it is still a challenging problem to purify the reaction product without damaging the tubes. Many methods have been developed for purification of SWNTs, including hydrothermal treatment [7], gaseous or catalytic oxidation [8, 9], nitric acid reflux [10–12], peroxide reflux [13], cross-flow filtration [14], and chromatography [15]. Purifications based on

an initial selective oxidation to remove amorphous carbon (and not induce serious loss of SWNTs), followed by refluxing in a concentrated acid with stronger oxidizing properties such as nitric acid, have also been found to be effective in removing metal catalysts from the reaction products [16–18]. However, refluxing in oxidizing solutions can induce wall damage in the tubes, and removing the carbon-coated residual catalyst without such wall damage remains a serious challenge. Obviously, the presence of defects in SWNTs will have an adverse impact on their various applications. Therefore, it is extremely important to explore a non-destructive purification route for SWNTs.

As a large-scale and economical synthesis method,

Address correspondence to Yunqi Liu, liuyq@iccas.ac.cn; Hisashi Kajiura, Hisashi.Kajiura@jp.sony.com



an electric arc discharge is one of the most efficient techniques to produce SWNTs with a high degree of crystallinity and low defect concentration [19, 20]. Although rare-earth (RE) elements have been extensively used together with Ni in bimetallic catalysts for improving the yield of SWNTs, their removal is arduous due to the complex experimental operations and the inertia of RE metals [21, 22]. In general, yttrium, as a metal catalyst for the growth of SWNTs in an arc discharge, is not easily removed by refluxing in mineral acids. Although most of the catalyst particles can be removed after reaction for a long time, the SWNTs are damaged in such a process. Applications of the resulting low-quality SWNTs will be restricted, especially in electronics. However, in classical coordination chemistry, it is well known that some aminopolycarboxylic acids (Fig. 1(a)) readily coordinate with yttrium to form complexes with high coordination numbers (Fig. 1(b)) [23]. During the reaction process, SWNTs should remain intact. In the present work, we selected a series of aminopolycarboxylic acids as ligands, including ethylenediaminetetraacetic acid (EDTA), trans-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid

(CYDTA), diethylenetriaminepentaacetic acid (DTPA), and triethylenetetraaminehexaacetic acid (TTHA), to remove the metal catalysts based on the coordination chemistry process. We found that this processing step allows the aminopolycarboxylic acids to efficiently coordinate with the metal catalysts without damaging the SWNTs. As a result, the conductivity of films based on the SWNTs was markedly improved in comparison with those prepared from SWNTs treated by oxidizing acids. This will further pave the way for applications of SWNT films in photovoltaic and electroluminescent devices [24].

1. Experimental

A conventional arc discharge was used for the preparation of SWNTs. In brief, the SWNT samples were obtained by arcing $YNi_{4.2}$ alloy-impregnated graphite rods in a helium atmosphere at a pressure of 550 torr. The cathode was a graphite rod with a diameter of 8 mm. The anodes were pure graphite rods with a diameter of 6 mm which were drilled and filled with a powdered mixture of $YNi_{4.2}$ and graphite ($YNi_{4.2}:C = 1:15$, atom ratio). The arc discharge was

run at a current of ~ 90 A and a voltage of 25 V. For the non-destructive purification of SWNTs, 10 mg of pristine samples were first annealed at 200°C for 10 h with an air flow of 20 mL/min in order to entirely oxidize the metal catalysts to their oxides. The samples were dispersed in deionized water using ultrasonic treatment for 30 min. Aqueous aminopolycarboxylic acid solutions (0.5 mol/L) were then added into the SWNTs solution. After the mixture was refluxed at 110°C for 18 h, the pH was adjusted to ~ 8 by using 1 mol/L NaOH. Subsequently the suspension was filtrated with a $0.5\text{-}\mu\text{m}$ -porous polytetrafluoroethylene filter and rinsed many times by hot water. Then the samples were dispersed in *o*-dichlorobenzene (*o*-DCB)

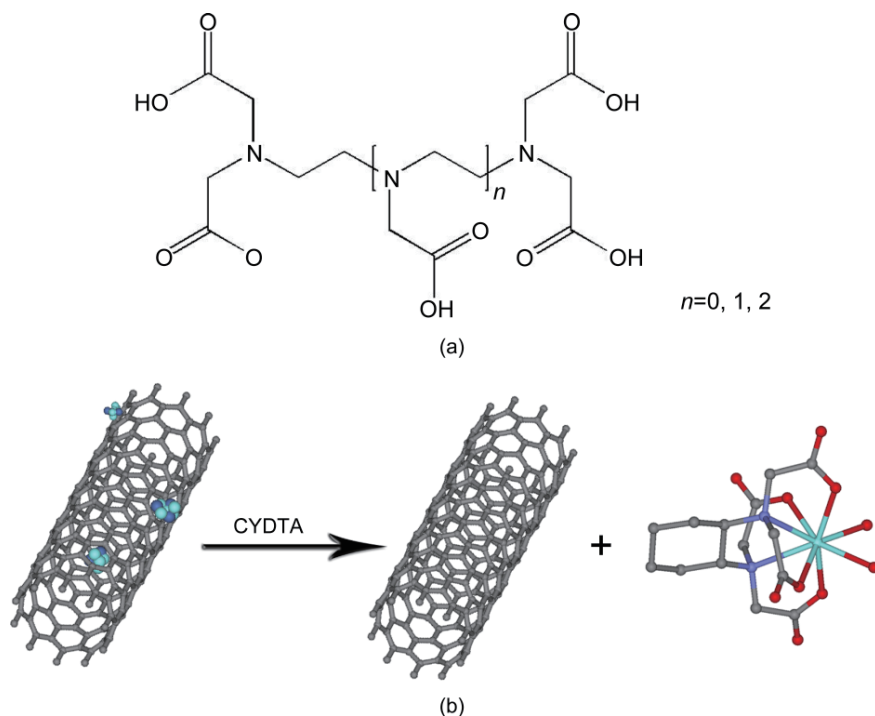


Figure 1 (a) Molecular structure of the aminopolycarboxylic acids EDTA ($n = 0$), DTPA ($n = 1$), and TTHA ($n = 2$). (b) A schematic illustration of the non-destructive purification of SWNTs by using CYDTA

and centrifuged at 18000 *g* for 3 h. The supernatant was decanted and collected *via* membrane filtration; the resulting sediment was used in the next resuspension/centrifugation/decantation cycle. Finally, SWNT films were fabricated by the filtration method with a mixed cellulose ester (MCE) filter membrane (Millipore, 0.2- μm pore) in a vacuum filtration apparatus (Millipore).

The samples were characterized by scanning electron microscopy (SEM, Hitachi S-4300F, 15 V) and transmission electron microscopy (TEM, Hitachi-2010, 200 kV). Raman spectra were recorded on a Renishaw 1000 micro-Raman system, with a charge-coupled device detector. A He-Ne laser with excitation energy of 1.96 eV (633 nm) served as excitation source, with a spot size of $\sim 1 \mu\text{m}$ in diameter. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCA-Lab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV. The purity of SWNT materials was measured on a thermal gravimetric analyzer (TGA, Dupont Instruments, 951 TGA), and the sample was heated to 800 °C at 5 °C/min in air. The sheet resistances of the SWNT films were measured in a low-resistivity meter with a 4-pin probe (Loresta-EP MCP-T360).

2. Results and discussion

Raman spectroscopy is a very powerful technique for characterizing SWNTs. The two most prominent features observed in the first-order resonant-Raman spectrum of SWNTs are the low-frequency radial breathing mode (RBM) located typically in the range 100–300 cm^{-1} and the high-frequency G band between 1500 and 1600 cm^{-1} which is composed of several tangential modes due to stretching vibrations of the SWNT sidewall carbon–carbon bonds. In addition, another peak around 1350 cm^{-1} , the D band, is associated with SWNT defects and amorphous carbon present as impurities. In general, the ratio of the G and D bands, *G/D*, is used to roughly gauge the defects and estimate the purity of the SWNTs [25].

First, we carried out the purification of SWNTs

with EDTA and CYDTA. The Raman spectra of the SWNT samples after the purification sequence are displayed in Fig. 2(a). All three characteristic spectral regions of SWNTs are essentially retained after the process. From the peaks in the RBM region, we can confirm the samples are SWNTs and estimate their diameter. The frequency of the RBM mode is inversely proportional to the diameter of the SWNTs, and the relationship can be described by $\omega = 234/d + 10$, where ω is the RBM frequency in cm^{-1} and d is the diameter of the SWNTs in nm, with consideration of the bundle effect [26]. The main peak at 198 cm^{-1} can therefore be attributed to carbon nanotubes with a diameter of 1.24 nm. At the same time, we can see that the *G/D* ratio in the sample purified using

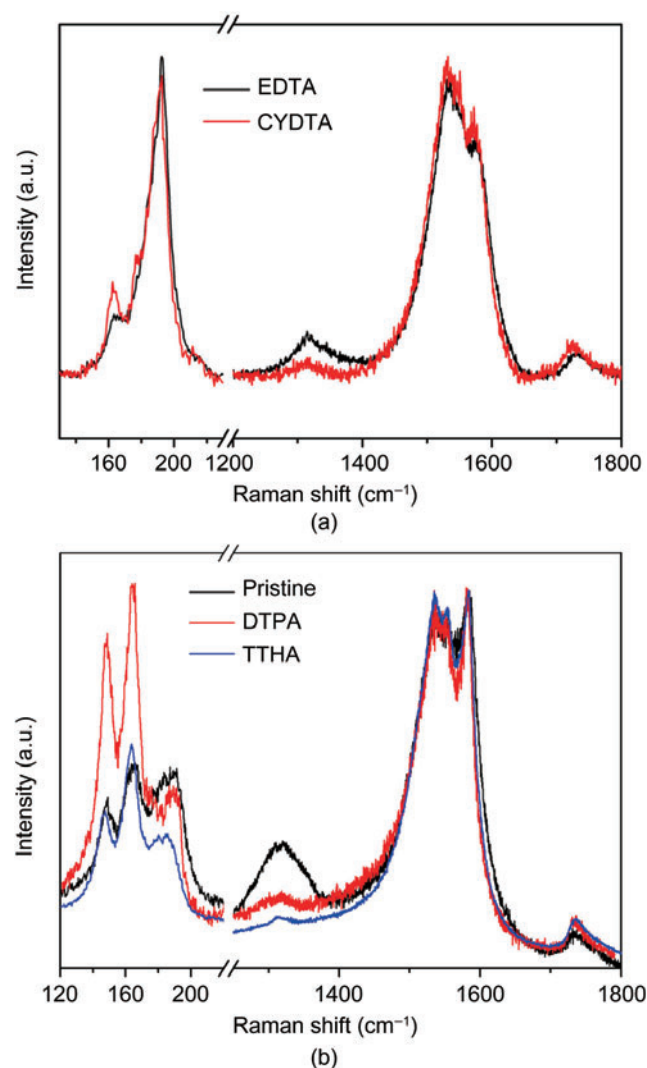


Figure 2 Comparison of Raman spectra of SWNTs after purification with different aminopolycarboxylic acids: (a) EDTA vs. CYDTA; (b) DTPA and TTHA vs. pristine SWNTs

CYDTA is larger than that in the sample purified using EDTA. This indicates that CYDTA is more effective than EDTA in non-destructive purification. The SWNTs become well segregated from the adsorbed amorphous carbon in the solutions after vigorous stirring under reflux conditions. It is known that nitrogen-containing functional groups, such as amines and amides, possess significant affinity for physi- or chemisorption with attendant weak charge transfer on the SWNT sidewalls due to the high nucleophilicity of these N-based groups. Hence, the amine adsorption on the nanotube wall, stabilized by the donation of π -electrons from the aromatic rings to the N-based electronegative moieties, should be the dominant interaction that drives the dispersion [27]. The presence of the six-membered cyclohexane ring in CYDTA will result in a much bigger repulsive force. Furthermore, for the same central metal ion, complexes based on CYDTA have higher stability constants than those based on EDTA [28]. These may be the reasons why CYDTA is more efficient than EDTA for the purification of SWNTs.

We also employed two other aminopolycarboxylic acids (DTPA and TTHA) with increasing numbers of amino groups to carry out the same purification procedure. From the Raman spectra in Fig. 2(b), both DTPA and TTHA were effective in the isolation and purification of SWNTs. The G/D ratios in the spectra of the purified SWNTs present a striking contrast to the value for the crude sample. We found that TTHA is the most promising ligand for the non-destructive purification of SWNTs. TTHA cannot only form binuclear nine-coordinate complexes with yttrium but also binuclear six-coordinate complexes with nickel [18, 29]. Figure 3(a) shows a typical SEM image of pristine SWNTs produced by the arc discharge method. After the non-destructive purification by TTHA, we can see that most of the impurities have been removed and only a small

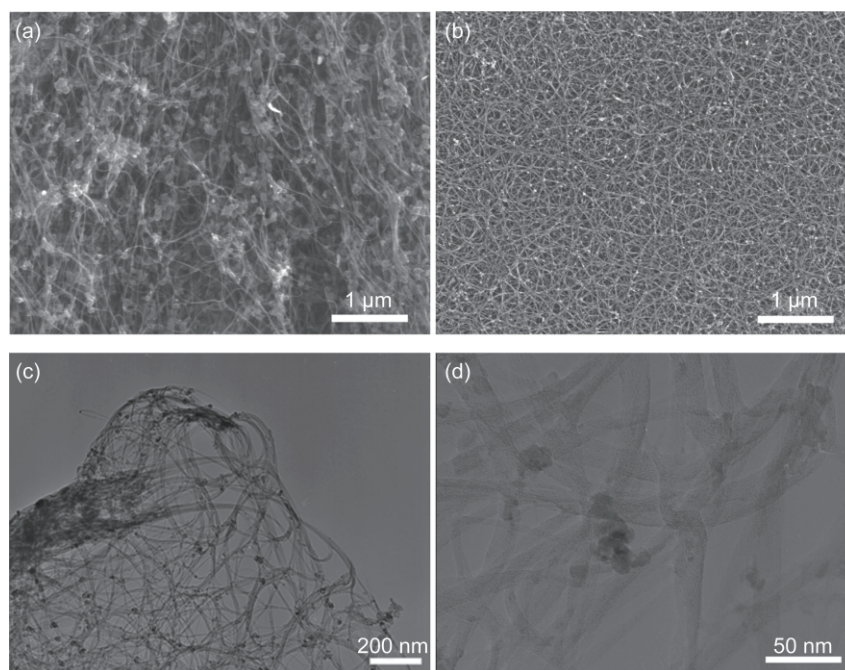


Figure 3 Microscopy characterization of SWNTs: (a) SEM image of pristine SWNTs; (b) SEM image of SWNTs after purification by TTHA; (c) TEM image of SWNTs after purification by TTHA; (d) TEM image from (c) at high magnification

amount of amorphous carbon still adheres to the SWNTs (Fig. 3(b)). From the TEM image in Fig. 3(c), it can be seen that the sample is essentially composed of bundles of SWNTs with some amorphous carbon. Earlier experiments have shown that the latter can be removed by ultracentrifugation without damaging the SWNT [30]. The high-magnification TEM image (Fig. 3(d)) shows that the sidewalls of the SWNTs are very smooth, which confirms that they are not damaged during the purification process.

XPS analyses were performed in order to better understand the difference between the conventional oxidizing acid treatment and our nondestructive purification process. The resulting XPS C 1s core spectra are shown in Fig. 4(a), in which the intensities of the strong C 1s peaks at 284.8 eV, which can be attributed to the sp^2 carbon atoms of the carbon skeleton, have been normalized to the same scale and also serve as a reference. The C 1s spectrum of SWNTs purified by refluxing in HNO_3 (3 mol/L) for 18 h was fitted to several symmetrical components according to the peak assignment used by Hiura et al. [31]. The three peaks in the high energy shoulder of the main peak, with binding energies located at 286, 287.4, and 289.1 eV, can be assigned to C–O (e.g.,

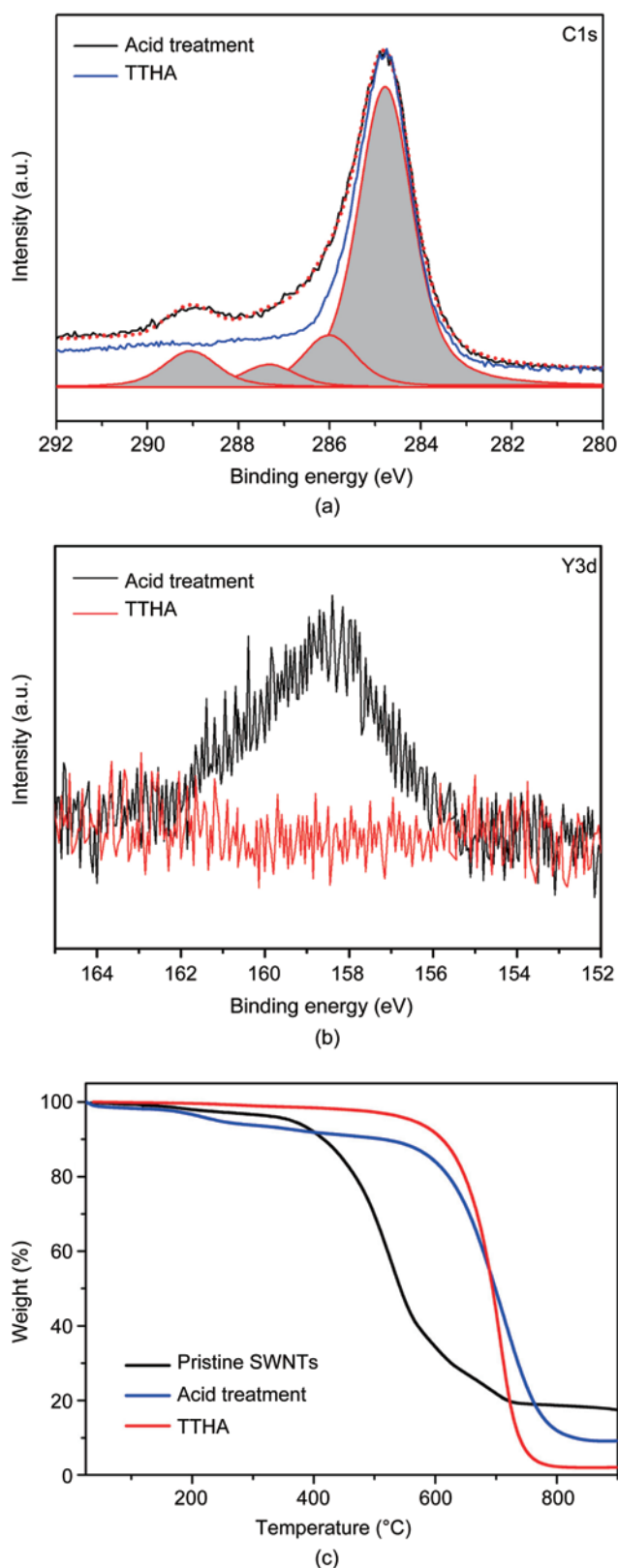


Figure 4 Comparison of XPS spectra and TGA traces of SWNTs purified by acid treatment and the TTHA process: (a) C 1s XPS; (b) Y 3d XPS; (c) TGA traces of the pristine SWNTs and those obtained by acid treatment and TTHA purification

alcohol and ether), C=O (e.g., ketone and aldehyde), and O–C=O (e.g., carboxylic acid and ester) species, respectively [32, 33]. These groups are introduced during the oxidizing purification of as-synthesized carbon nanotubes. The Y 3d spectra of the SWNTs purified by the two processes are compared in Fig. 4(b). We did not detect any yttrium signal after the coordination chemistry process, while traces of yttrium remain after the acid reflux treatment. From the TGA trace in Fig. 4(c), the purity of SWNTs was increased from 80.5% to 98.2% after purification *via* the TTHA process, while the purity of the counterpart after acid treatment only reached 90.5%. We suggest that the oxygen-species formed on the SWNTs in the latter case are responsible for the residual metal. Rare earth metal ions coordinate preferentially to oxygen donors rather than to nitrogen donors [34]. This will lead to competition for the catalyst metals between the aminocarboxylic acid ligands and the grafted functional groups on SWNTs.

Finally, using the samples purified by TTHA, we fabricated transparent and conducting SWNT films based on a filtration method (see the inset of Fig. 5) [24]. Compared with the films made of SWNTs refluxed in HNO₃, the sheet resistances of films of SWNTs obtained by our non-destructive purification method are significantly reduced (Fig. 5). Even for SWNT films on flexible polyethylene terephthalate (PET) substrates, their conductivity is clearly superior

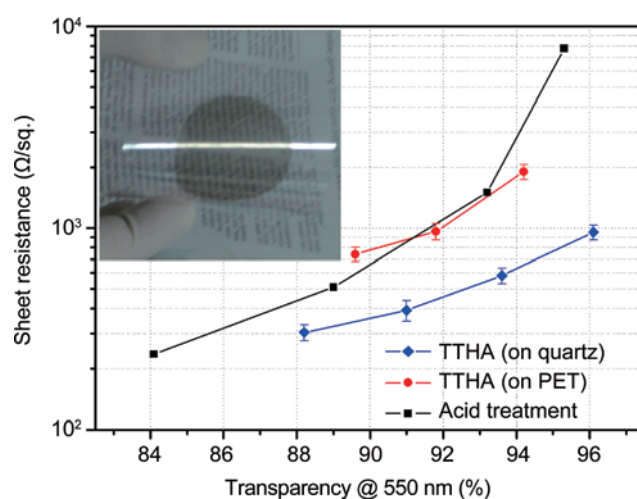


Figure 5 Comparison of sheet resistance vs. transparency curves of the SWNT films fabricated from nanotubes obtained by acid treatment and the nondestructive method using TTHA. The inset is a photograph of the SWNT film on a flexible PET substrate

to that of the acid-treated samples. This comparison was, however, made with as received HNO₃-refluxed SWNT material which had not been purified to the same degree as our aminopolycarboxylic acid-treated materials. This could also explain the differences seen. Further studies are needed for a more definitive conclusion. It can be predicted that the conductivity of SWNT films will further be improved after other relevant optimization such as chemical modification of the films, increasing the length of the tubes, orientational alignment of the tubes, raising the purity of SWNTs, and so on. This research is currently underway.

3. Conclusions

We have developed a non-destructive purification route for SWNTs based on classical coordination chemistry using a series of aminopolycarboxylic acids to remove the metal catalyst. The molecular structure of the ligands and the number of amino groups affect the performance of the ligands in the purification process. TTHA was found to give the best performance. Moreover, because defects are absent, the conductivity of films based on SWNTs purified by the non-destructive process is significantly better than that of films obtained using acid-treated SWNTs. If the non-destructive purification process can be combined with other processes to control the diameter and length of the SWNTs and the preparation of the film, it should be possible to optimize the conductivity of SWNT films. We believe such films will find widespread applications in future nanoengineering and nanotechnology, particularly in optoelectronic applications.

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