

A Highly Selective, One-Pot Purification Method for Single-Walled Carbon Nanotubes

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We report on a one-pot, highly selective chemistry to remove residual catalysts from single-walled carbon nanotubes (SWNTs). The impurities, initially present at ~35 wt % and mostly as carbon-coated iron nanoparticles, can be driven below 5 wt % with nearly no loss of SWNTs. The carbon-coated iron impurities are dissolved simply by reacting with an aqueous mixture of H₂O₂ and HCl at 40–70 °C for 4–8 h. This purification combines two known reactions involving H₂O₂ and HCl, respectively; however, by combining these two typically inefficient reactions into a one-pot reaction, the new process is surprisingly selective toward the removal of the metal impurities. This high selectivity derives from the proximity effect of the iron-catalyzed Fenton chemistry. At pH ~1–3, iron is dissolved upon exposure, avoiding the otherwise aggressive iron-catalyzed digestion of SWNTs by H₂O₂. This extremely simple and selective chemistry offers a “green” and scalable process to purify carbon nanotube materials.

Processes for making single-walled carbon nanotubes (SWNTs) are being scaled up to meet the growing demand induced by many emerging applications.¹ Most of such applications (e.g., thin transparent film devices² and any biological and medical applications³) require high-purity material with minimal metal residues. The HiPco process^{4,5} is currently the method of choice for making large amounts of high-quality SWNTs. However, as-produced HiPco materials typically contain ~35 wt % impurities, primarily consisting of iron nanoparticles (catalysts that did not sprout SWNTs) enclosed in carbon shells.^{6,7} Similar catalyst residues also contaminate SWNTs produced by most other methods.⁷ A variety of purification methods have been developed; however, removing impurities with high selectivity has been challenging because the carbon shells and the SWNTs have similar reactivities.^{7,8} Most of the purification methods exploit gas phase oxidation with O₂, CO₂, or H₂O vapor at elevated temperatures (300–800 °C),^{6,9,10} or wet chemical oxidation with oxidants including nitric acid, H₂O₂, or KMnO₄. These aggressive processes typically damage SWNTs severely; particularly, HiPco SWNTs can be completely destroyed by wet oxidative methods^{11–13} that are developed for SWNTs produced by arc discharge or laser oven.^{7,8} Recent reports have shown that both the carbon yield¹⁴ and purity¹⁵ can be significantly improved by selectively heating the metal residues with microwaves¹⁶ or by exploiting metal-catalyzed oxidation at

150–425 °C.^{6,9} The carbon yield of the latter is improved to nearly 70% by deactivating the exposed iron and iron oxide catalysts with C₂H₂F₄ or SF₆, but this process requires time-consuming multiple steps, high-temperature oxidation, and environment-harmful reagents.⁹ Despite the utmost practical interest, highly selective and environmentally benign purification approaches have yet to be developed.

Here, we report a one-pot, solution phase reaction with excellent selectivity toward the removal of the carbon-coated iron nanoparticles from HiPco materials. By heating the raw materials at 40–70 °C in an aqueous mixture of H₂O₂ and hydrochloric acid, the iron impurities are dissolved, leaving SWNTs largely intact. Our process combines two known reactions: oxidation of raw carbon nanotube materials by H₂O₂ and removal of metals by hydrochloric acid. These two reactions are typically carried out sequentially or separately.^{2,17–20} We demonstrate that combining these two reactions into a single pot simplifies the process and, surprisingly, improves the carbon yield and the product purity. Hydrochloric acid itself cannot remove most metal impurities from raw HiPco materials because of the carbon coating. While H₂O₂ alone has been used in the past to purify carbon nanotubes including HiPco materials, the process has thus far resulted in very limited success.^{17–19} The major problem is that SWNTs are substantially consumed by H₂O₂, resulting in extremely low yields (in some cases as low as 1%).^{17–20} By lowering the pH to ~1–3, we found that the carbon yields can be significantly increased to over 75% with a purity up to 96 wt %; the major carbon loss is due to the carbon coatings and ~5–10 wt % giant fullerenes²¹ in the raw HiPco materials.

This unusually high selectivity derives from two important novel features in our process. First, the metal impurities act as

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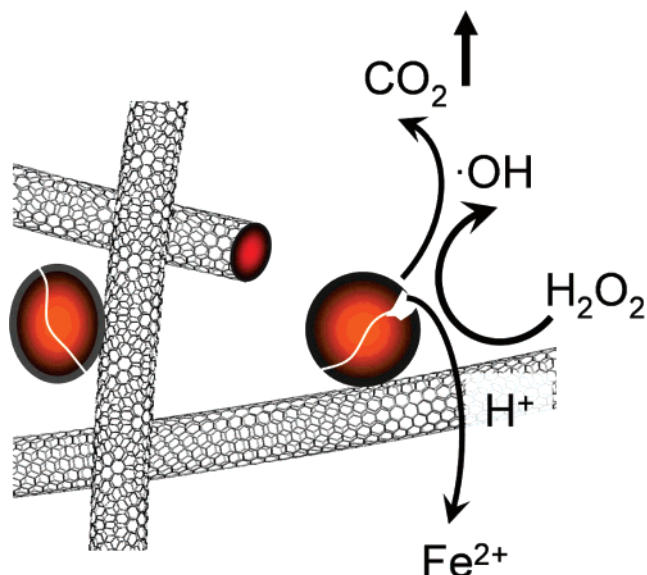


Figure 1. Schematic of the localized catalytic reaction of H_2O_2 with carbon-coated iron nanoparticles (not drawn to scale).

a catalyst to effect the purification via Fenton's chemistry.²² Fenton's chemistry is known to produce hydroxyl radicals ($\bullet\text{OH}$), a more powerful oxidant than H_2O_2 . Without metal catalysts, H_2O_2 alone has almost no effect on purified SWNTs under our reaction conditions, as is evident by control experiments that show negligible mass loss of SWNTs. These observations suggest high reactivity of $\bullet\text{OH}$ toward the destruction of carbon coatings, which typically requires oxidation at high temperatures ($>300\text{ }^\circ\text{C}$) for a gas phase purification process.^{6,9} Presently, we cannot determine whether and how H_2O_2 can breach perfect carbon shells. However, most of the carbon coatings that enclose an iron nanoparticle are not perfectly closed graphitic shells.⁶ We speculate that H_2O_2 can penetrate the shells through imperfections and combine with the enclosed iron to promote the digestion of the carbon coating. Second, unlike previous attempts^{17–19} which use H_2O_2 alone, our process adds hydrochloric acid to dissolve the iron nanoparticles upon their exposure. The exposed iron is released as ions and quickly diffuses into solution, thereby eliminating iron and iron hydroxide precipitations and their unwanted catalytic effect in the consumption of SWNTs (Figure 1). Although the released Fe^{2+} still catalyzes Fenton's chemistry, it becomes a homogeneous catalyst in the solution²³ and poses minimal damage to SWNTs because of the short half-life (nanoseconds)—and hence diffusion length of hydroxyl radicals²⁴—and minimal exposed surface of SWNTs due to the roping effect (SWNTs densely packed into a rope with a cross section consisting of up to ~ 200 SWNTs). Therefore, by confining the catalytic effect to the vicinity of the carbon-coated iron nanoparticles, both high selectivity in removing the iron impurity and low consumption rate of SWNTs are accomplished. While the data presented here focus on the purification of HiPco materials, this method should be readily applicable to other carbon nanotube materials that contain a metal (e.g., iron or cobalt) to catalyze Fenton's chemistry.

Experimental: A 20–50 mg portion of fluffy raw HiPco materials (lot 112.1) was mixed directly with 20 mL of 1 N hydrochloric acid and 20 mL of 30% H_2O_2 in a 250 mL open flask and stirred with a magnetic stirrer at 600 rpm to form a slurry. (**Caution: H_2O_2 is a strong oxidizer. Contact with skin may cause irritation.**) This slurry was heated on a hot plate and held at $60 \pm 5\text{ }^\circ\text{C}$ for 4 h. At the end of each hour,

20 mL of hydrochloric acid and 20 mL of H_2O_2 were added to the slurry. On the last cycle, one additional hour was allowed to completely decompose H_2O_2 . Within the first 30 min, the solution turned green/yellow colored, indicative of iron dissolution. Interestingly, after stopping the reaction, the SWNTs floated as a distinct layer on the clear yellow solution, which allowed physical separation simply by decanting off the aqueous solution. The isolated SWNTs were then collected over a filter paper and washed with 500 mL of nanopure water. The samples were dried at $120\text{ }^\circ\text{C}$ in air for 2 h, weighed, and characterized with standard techniques²⁵ including transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Raman spectroscopy. The control sample was prepared and characterized following the same procedure but with reduced reaction time (0.5 h each cycle) and using water in the place of hydrochloric acid.

TEM images before and after purification show clearly the effectiveness of the purification process. Most iron impurities, initially present as 2–7 nm nanoparticles (Figure 2a), are removed, yielding purified SWNT materials essentially free of metals and giant fullerenes²¹ (Figure 2b). In contrast, SWNTs are covered with iron hydroxides after reacting with H_2O_2 only (Figure 2c). The corresponding iron contents (weight % of Fe, converted from Fe_2O_3 recorded by TGA) of the raw, purified, and control samples are determined from TGA measurements in flowing air (Figure 3) to be 35 ± 3 , 4.6 ± 0.7 , and 56 ± 4 wt %, respectively. The purity improved consistently as the time of the purification reaction increased up to 8 h, and the yield remains at a high level (carbon yield $>75\%$).

The selectivity of this chemistry is further supported by the corresponding Raman spectra (Figure 4). In these experiments, a 632.8 nm excitation line was chosen because it probes both large diameter metallic nanotubes and smaller diameter semiconductors, therefore providing an estimate of the changes in the relative populations of various SWNTs (e.g., metallic vs semiconducting) due to the reaction. The Raman spectra of the purified SWNTs show that the G-bands are preserved and the D-band increases minimally in comparison with the raw material spectra, indicating little sidewall damage due to the $\text{H}_2\text{O}_2/\text{HCl}$ purification. Surprisingly, even when reacting with H_2O_2 alone, the SWNTs that survive the reaction show persistent G-band and radial breathing modes (RBMs) and a nearly unchanged relative intensity of the D-band. These observations suggest that SWNTs were attacked by H_2O_2 primarily from the nanotube ends and few new sidewall defects were introduced in this purification process. This result is consistent with the superior performance of electronic devices made of H_2O_2 -purified SWNTs.² However, Raman spectroscopy is insensitive to probe low degrees of sidewall damage; more direct evidence, such as from scanning tunneling microscopy studies, are required to quantify the degree of the structural integrity of the purified SWNTs.

After the $\text{H}_2\text{O}_2/\text{HCl}$ purification [$\text{SWNTs} + \text{Fe} + \text{H}_2\text{O}_2 + \text{HCl}$], the relative intensity of the Breit–Wigner–Fano (BWF) component in the G-band increased, but the increase was much less significant in comparison with previous findings where the reaction occurs between purified SWNTs and H_2O_2 under light radiation²⁶ or at $\geq 90\text{ }^\circ\text{C}$.²⁷ In these two previous experiments, it was suggested that the reactions caused enrichment of metallic SWNTs. The relatively small change in the relative Raman intensity from our samples, however, indicates that SWNTs barely react with $\text{H}_2\text{O}_2/\text{HCl}$ under our purification conditions. Indeed, side-by-side comparison experiments showed that room light had no appreciable effect on the reaction rates of various

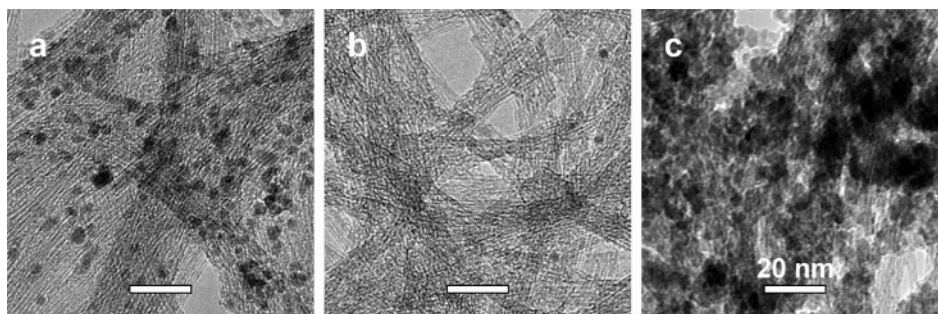


Figure 2. Representative TEM images of (a) raw HiPco materials and after reacting with (b) $\text{H}_2\text{O}_2/\text{HCl}$ for 4 h and (c) $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ for 2 h (control).

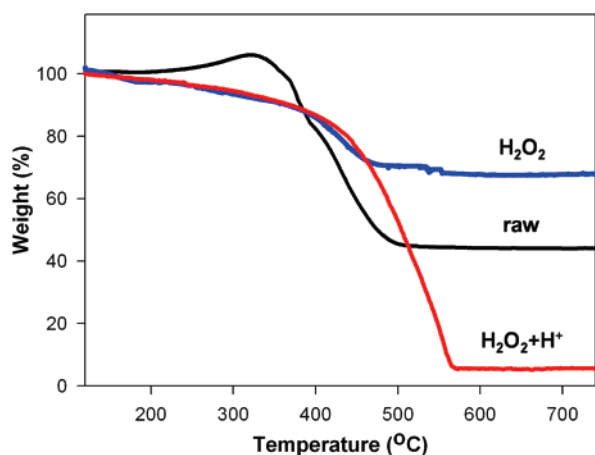


Figure 3. TGA curves showing that the corresponding ash contents (Fe_2O_3) are reduced from 44 wt % (raw) to 6.5 wt % (purified), whereas they increase to 65 wt % after reacting with H_2O_2 alone due to the consumption of SWNTs (control).

reactions involving SWNTs and H_2O_2 (with or without iron and HCl , at 20–70 °C). Importantly, the reactivity of purified SWNTs with H_2O_2 [reaction of SWNTs + H_2O_2] depends strongly on temperature: below 60 °C, the reaction is barely observable (this experiment); however, at 90 °C, enrichment of metallic SWNTs is reported.²⁷ This temperature dependence is similar to a previously reported experiment involving 4:1 (vol/vol 96% H_2SO_4 /30% H_2O_2) piranha, which showed that at room temperature SWNTs are consumed from the ends (with little sidewall damage), whereas they are cut to short pieces at 70 °C.²⁸ Therefore, we conclude that the main cause of the significant SWNT loss in the H_2O_2 -involved purification reported previously^{17–19} arises from the catalytic effect of iron,

which catalyzed the production of $\bullet\text{OH}$ from H_2O_2 . Indeed, in the absence of hydrochloric acid, raw HiPco material was completely consumed by H_2O_2 within 5 days at room temperature or 3 h at 60 °C [reaction of SWNTs + Fe + H_2O_2]. However, in the absence of iron (purified samples), SWNTs survived without appreciable mass loss under both conditions [reaction of SWNTs + Fe + H_2O_2 + HCl].

The experiments reported here were designed to elucidate the chemistry of this purification technique. However, from the technology perspective, there is plenty of room for optimization. For example, a similar purity and yield of SWNTs were obtained when adding a filtration step between the sequential additions of $\text{H}_2\text{O}_2/\text{HCl}$, suggesting the possibility of automated stepwise additions of reactants. Purity and yield could be improved further by tuning the reaction temperature, pH, and concentrations of Fe^{2+} and H_2O_2 . Nevertheless, the level of purity achieved in our preliminary experiments is sufficient to allow the use of SWNTs in many advanced applications such as composite materials and transparent, conductive thin films.¹

In summary, this work provides an impurity-catalyzed, one-pot reaction to reduce iron impurities in HiPco SWNTs from ~35 wt % (raw material) to below 5 wt % with nearly no loss of SWNTs. This novel method combines in a single step oxidation involving H_2O_2 and metal extraction with hydrochloric acid, which are normally performed separately. The iron impurities become an effective catalyst for Fenton's chemistry through its in situ change of its chemical state from Fe to Fe^{2+} by hydrochloric acid. The mixed $\text{H}_2\text{O}_2/\text{HCl}$ reagents display unusually high selectivity toward the removal of iron and other non-nanotube impurities; they do not destroy SWNTs because the iron nanoparticles catalyze the H_2O_2 attack to the carbonaceous shells but quickly dissolve by acid and diffuse to the

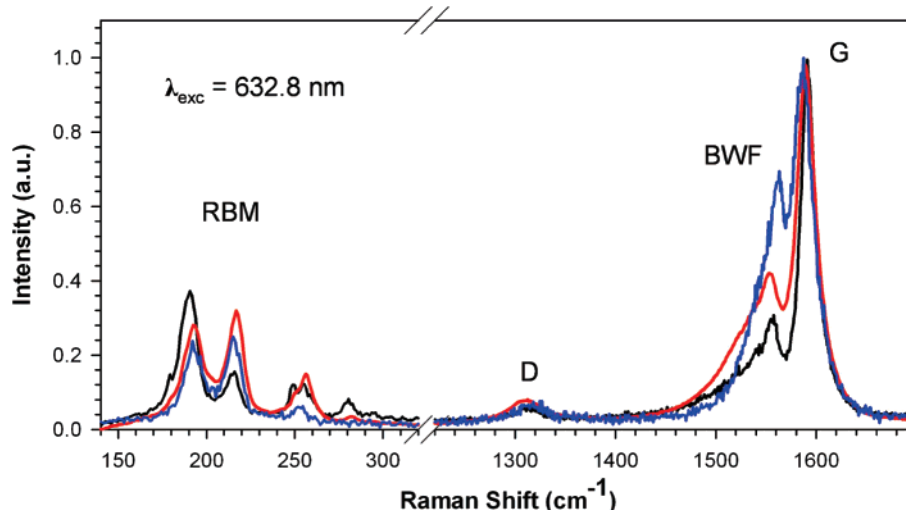


Figure 4. Raman spectra of the corresponding HiPco materials: raw (black line); purified (red line); control (blue line).

solution before they can come in contact with the SWNTs. The key advantages of this method are that it is solution-based, relies on a simple setup operating at low temperature, and uses H₂O₂, an inexpensive green oxidant²⁹ widely used for wastewater treatments,³⁰ and HCl, a widespread chemical that can be easily converted into harmless salt (e.g., NaCl). Such advantages clearly make this method an excellent candidate for scaling into an industrially viable process for carbon nanotube purification.

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- (14) Note: The carbon yield is defined as the percentage of the purified SWNTs to the carbon content of the starting raw material.
- (15) Note: The purity is defined as the carbon content of the purified material. The absolute purity of SWNTs is not defined here because the absolute amount of non-SWNT carbon is difficult to quantify. For a recent advance toward a standard quantification method, see ref 8.
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