Stable Containment of Radionuclides on the Nanoscale by Cut Single-Wall Carbon Nanotubes

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The physisorption of radiolabeled ¹²⁵I⁻ ions from aqueous solution and the Brunauer–Emmett–Teller (BET) surface areas of various carbonaceous materials [HiPco single-wall carbon nanotubes (SWNTs), F-SWNTs, cut SWNTs, charcoal, graphite, F-graphite and C₆₀] have been measured and compared. By far, cut SWNTs (mainly 20–50 nm lengths) displayed the largest surface area of the materials (1180 m²·g⁻¹), being approximately double that of uncut SWNT and charcoal. At low concentrations of ¹²⁵I⁻, nearly all of the ¹²⁵I⁻ was adsorbed from aqueous solution within 1 min at room temperature by the cut SWNTs, uncut SWNTs, and charcoal; the other materials showed much less adsorption under the same conditions. Once adsorbed, the ¹²⁵I⁻ wash-off rate by pure water was highly variable but was especially slow for cut SWNTs ($t_{1/2} \approx 2720$ h) compared to the other materials; wash-off of ¹²⁵I⁻ by an aqueous H₂O₂ solution (¹²⁵I⁻ $\stackrel{H_2O_2}{\longrightarrow}$ 1²⁵I₂) was even slower ($t_{1/2} \approx 14300$ h). Taken together, these data demonstrate the greatly increased surface area and dramatically enhanced retention properties of cut SWNTs over uncut SWNTs.

The surface area of single-wall carbon nanotubes (SWNTs) has been of special interest recently because of the potential of this material to store and transport H₂ economically.^{1,2} In this paper, we report that the surface area of pristine HiPco SWNTs can be approximately doubled by "cutting" the material into 20–50 nm length via the fluorination/pyrolysis procedure reported by Margrave and co-workers.³ In addition, the adsorption/desorption properties of these cut SWNTs and uncut SWNTs have been further compared by use of adsorption/ desorption data for radiolabeled ¹²⁵I⁻ ions and ¹²⁵I₂ molecules in aqueous solution.

The HiPco SWNTs used in this investigation were obtained from Carbon Nanotechnologies, Inc. of Houston, Texas (iron content ~12%). Fluorination of the SWNTs was performed as previously reported (on the same fluorination apparatus)³ at 100 °C for 2 h and at a He:F₂ ratio of 99:1. The resulting fluorinated nanotubes (F-SWNTs), with a composition between C₈F and C₆F, were observed to slowly evolve HF (etching the sample bottle) in air over several days, so only freshly prepared F-SWNTs were used for the "cutting" procedure by pyrolysis under argon at 1000 °C for 1 h. As reported by Margrave and co-workers,³ this procedure results in cut SWNTs with lengths ranging mainly between 20 and 50 nm.

The surface areas of the cut and uncut SWNTs were then measured at 77 K with a Micromeritics ASAP 2010 Brunauer– Emmett–Teller (BET) surface analysis instrument that used N_2 gas. For comparison, similar measurements were also performed for F-SWNT, charcoal (Fisher Scientific), graphite (Aldrich Chemical Co.), F-graphite (Aldrich Chemical Co.; white color, average composition C_2F) and C_{60} fullerene (MER Corporation, 99.5+ % purity). The results are summarized in Table 1.

As seen in Table 1, the measured BET surface area for cut SWNTs of 1180 $m^2 \cdot g^{-1}$ is approximately double that of uncut SWNT (and charcoal). Our value of 675 $m^2 \cdot g^{-1}$ for the surface area of uncut SWNT is within the range of previous results in the literature.^{4,5} It is tempting to speculate that the increase in surface area from "cutting" SWNTs into shorter lengths arises from greater access to the interior walls of the cut tubes because of side-wall damage (and possibly end opening) during the fluorination/pyrolysis procedure. Side-wall damage is clearly evidenced by Raman spectroscopic data³, and it is reasonable that such damage would create openings large enough for small molecules (N_2, F_2, H_2) to efficiently enter cut nanotubes. Alternately, the cut SWNT may simply be debundled to a greater extent than uncut nanotubes, and the increase in surface area for the cut nanotubes is due to a larger available outside surface area. However, we tend to favor the "side-wall damage" explanation because (1) the ${}^{125}I^{-/125}I_2$ radiotracer study given below demonstrates a greatly enhanced retention capability for only the cut nanotube adsorbent in Table 1, (2) strongly sonicated (at 500 W) and unsonicated samples gave identical surface areas for cut and uncut SWNT samples, even though sonication is known to debundle SWNTs,^{9,10} and (3) we have been able to internally load I₂ into cut SWNTs (up to 40% I₂ by weight) either by sublimation or from a I₂/CHCl₃ solution.^{11,12}

An aqueous solution of Na¹²⁵I (AmerSham) was used to obtain a solution in the concentration range of $10^{-9}-10^{-12}$ mol·L⁻¹. Each insoluble carbonaceous substance (1.0 mg) was then added, with stirring, to 1 mL of HPLC-grade water containing 2.79×10^{-14} mol of $^{125}I^-$. In a typical adsorption experiment, the carbonaceous material was removed by filtration after 1 min and the amount of $^{125}I^-$ remaining in solution and

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TABLE 1: BET Surface Areas for Carbonaceous Materials

adsorbent	surface area, ^{<i>a</i>} m ² ·g ⁻¹	lit. value	ref
cut-SWNT	1180		
uncut SWNT	675	266-800	4, 5
charcoal	632	$400 - 900^{b}$	8
F-SWNT ^c	220		
F-graphite	155	110	6
graphite	5.88	4.31-6.22	7
C ₆₀	0.127		

^{*a*} This work; max estimated error is 10%. ^{*b*} For most commercially available brands. ^{*c*} Freshly prepared sample.

TABLE 2: Adsorption of $^{125}I^-$ from Aqueous Solution by Carbonaceous Materials after 1 min at RT

adsorbent	$^{125}\mathrm{I}^-$ amount adsorbed, a %
cut-SWNT	99.7 ± 0.8^{b}
charcoal	98.4 ± 1.5^{b}
uncut SWNT	95.2 ± 1.4^{b}
F-SWNT ^c	67.4 ± 1.7^{b}
graphite	6.51 ± 1.8^{d}
F-graphite	1.96 ± 1.4^{d}
C_{60}	1.05 ± 0.9^{d}

^{*a*} Data for eight or more experiments for all except graphite, F-graphite, and C₆₀, which had three experiments. ^{*b*} Standard deviation (σ) is 0.28% for cut SWNT, 0.49% for charcoal, and 0.46% for uncut SWNT. The errors given are 3 σ (95% confidence). ^{*c*} Freshly prepared sample. ^{*d*} The errors given are the range of three experiments.



Figure 1. Adsorption of ${}^{125}I^-$ from aqueous solution vs cut SWNT: ${}^{125}I^-$ molar ratio. To estimate the ratio, a cut SWNT length of 50 nm with MW = 115 000 was assumed.

the amount in the solid material were measured on a γ counter. Cut SWNTs exhibited the greatest adsorption of 99.7% with similar results for charcoal (98.4%) and uncut SWNTs (95.2%), while the other carbonaceous materials adsorbed far less of the radiotracer ion under the same conditions. The results are summarized in Table 2. Adsorption levels were also found to decrease as the ratio of adsorbent:¹²⁵I⁻ decreased, as displayed in Figure 1 for the case of cut SWNTs.

After adsorption of ¹²⁵I⁻, the carbonaceous materials (charcoal and cut and uncut SWNTs) were placed on a 4 mm polytetrafluoroethylene (PTFE) filter (Aldrich) and washed with HPLC-grade water, an unlabeled aqueous NaI solution $(10^{-2} \text{ mol}\cdot\text{L}^{-1})$, or an aqueous H₂O₂ solution $(10^{-3} \text{ mol}\cdot\text{L}^{-1})$. In the experiments, a 6 mL·day⁻¹ flow rate of each solution was used, and the activities of the PTFE filters and portions of the wash solutions were measured separately by a Packard Cobra-2, Auto-Gamma counter at 20 and 40 min and 1, 2, 4, 24, and 48 h intervals. From these data, desorption plots (time vs ¹²⁵I⁻ loss



Figure 2. Desorption rate of ¹²⁵I⁻ by pure water.







Figure 4. Desorption rate of ${}^{125}I^-$ by H_2O_2 solution.

rate, which is calculated by dividing the washed-out fraction of $^{125}I^-$ by time) were constructed as shown in Figures 2–4. The lines in the figures are linear least-squares fits of the data points and the error bars shown are the ranges obtained for four data points taken at each time (days). The resulting half-lives, $t_{1/2}$, for the desorption processes of Figures 2–4 are summarized in Table 3.

TABLE 3: Half-Lives for Desorption of $^{125}I^-$ by the Aqueous Solutions at a 6 mL·Day⁻¹ Wash-off Rate

	$t_{1/2},\mathbf{h}^{a,b}$		
adsorbent	water	aq NaI soln	aqueous H2O2 soln
cut-SWNT	2720	422	14300
uncut SWNT	54	14	147
charcoal	81	14	309

^{*a*} Each entry in Figures 2–4 is the average of four readings. ^{*b*} Max estimated error is 8%: instrument error (5%) plus weighting error (3%).

The rate of ¹²⁵I⁻ wash-off by the NaI solution was found to be 4-7 times higher than for pure water, which can be explained by an equilibrium competition between I⁻ from NaI and ¹²⁵I⁻ from Na¹²⁵I (common-ion effect). The further dramatic decrease in the desorption rate caused by a aqueous H₂O₂ solution is attributed to the oxidation of I^- to I_2 by H_2O_2 , with I_2 having a much greater tendency to adsorb to (and likely within) cut SWNTs than the I⁻ ion.^{13,14} Oxidation of I⁻ to I₂ within a cut SWNT would be one of the first documented examples of the chemical reaction occurring within the confines of a carbon nanotube structure. It was found that cut SWNTs have, by far, the slowest ¹²⁵I⁻ release rate of any of the carbonaceous materials. For example, charcoal lost ¹²⁵I⁻ approximately 30 times faster than cut SWNTs during the water or NaI solution wash-off procedure. Even more impressive, however, is the fact that conversion of ${}^{125}I^-$ to ${}^{125}I_2$ by the H₂O₂ solution increased the desorption half-life of I_2 in aqueous solution to 14 300 h or almost 2 years!

In summary, the present BET surface area and radioisotope adsorption/desorption investigation has revealed that cut SWNTs possess greatly enhanced surface area and retention properties relative to uncut SWNTs and other carbonaceous materials, making them the likely carbon-based material of choice for applications¹⁵ such as (1) H₂ storage/transport, (2) environmental radionuclide cleanup, and (3) radionuclide delivery in medicine.

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