

Supplementary material: AnnHyg-13-0016. Birch ME, Ruda-Eberenz TA, Chai M, Andrews R, Hatfield R. *Properties that Influence the Specific Surface Areas of Carbon Nanotubes and Nanofibers*

BET Analysis Parameters and Quality Assurance

The analysis procedures used by the two laboratories were as follows:

Laboratory 1 – A Micromeritics Gemini 2375 instrument was used to make 5-point, BET surface area measurements by nitrogen gas adsorption, with liquid nitrogen as the cryogen, at relative pressure points P/P_0 of 0.05, 0.10, 0.15, 0.20, and 0.25. Samples were degassed under flowing, ultra high purity (UHP) grade nitrogen for 30 minutes at 90 °C and 90 minutes at 200 °C.

Laboratory 2 – A Micromeritics TRiStarII 3020 instrument was used to make 5-point, BET surface area measurements using the same parameters as laboratory 1. Specifically, at P/P_0 points of 0.05, 0.10, 0.15, 0.20, and 0.25, with samples first degassed under flowing UHP grade nitrogen for 30 minutes at 90 °C and 90 minutes at 200 °C. A 50-point nitrogen isotherm analysis also was performed on two samples to determine surface area (and average pore size and single-point total pore volume at a $P/P_0 = 0.99$). Several samples were reanalyzed by the same method, but with sample preparation at 300 °C for 90 minutes rather than at 200 °C. Analyses also were performed after heating at 100 °C (90 minutes).

An ASTM carbon black (ASTM D24 SRB B-8 carbon black) of known SSA was included with the sample sets. For the two laboratories, the mean result ($n = 3$, RSD = 1%) for the ASTM material was 140.7 m²/g, which is within about 1% of the reported value of 142.6 m²/g.

Sample mass was typically 200 mg or more, with a minimum of 100 mg. Several materials were analyzed at two different laboratories, six months apart. Some samples were analyzed twice by the same laboratory (laboratory 2), with the second analysis being performed several months after the first. A 50-point isotherm analysis (laboratory 2) was performed on two samples previously analyzed by 5-point BET.

To examine the possible influence of degassing temperature, several samples were reanalyzed (laboratory 2) by the same method, except that the samples were heated at 300 °C for 90 minutes rather than 200°C. Analyses also were performed after degassing at 100 °C, to confirm that degassing at 200 °C produced no changes (e.g., melting and coalescence of metallic nanoparticles) in the materials that may have affected the results. Such changes were not anticipated because of the much higher temperatures normally used during CNT synthesis and processing.

As indicated in the tables below, all repeat analyses were in good agreement. Analytical precision for repeat analyses, by the same procedure at the same or at two different laboratories, was better than 4% (Table S1). Correlation coefficients (r^2) for BET fits were typically 0.9999 or better, with no value less than 0.9998.

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Heating at 300 °C and 200 °C for 90 minutes gave comparable results (Table S2), as did the 5-point BET and 50-point isotherm analyses (Table S3). Sample preparation at 100 °C gave lower (some slightly) surface areas than at 200 °C (Table S4), which is attributed to incomplete pore clearing of condensates. Degassing was therefore performed at 200 °C to ensure removal of adsorbed condensates.

Table S1. Analytical precision for repeat BET analyses at the same or two different laboratories.

sample	material	laboratory 1 BET SSA, m ² /g	laboratory 2 BET SSA, m ² /g	RPD ^a
31	SWCNT	662	677	2.2
21, 22 (same material)	SWCNT	–	802.0, 815.0	1.6
23	MWCNT	–	196.3, 200.2	2.0
24	MWCNT (high purity)	–	191.9, 193.6	0.9
9, 27 (same material)	MWCNT	–	290.0, 287.5	0.9
32	MWCNT (Mitsui)	22.0	22.5, 23.0	2.2 ^a
33	carbon black (ASTM)	139.8	139.3, 142.9	0.01 ^a
119	CNF-2	19.4	18.9	2.6
120	CNF-3	34.6	33.3	3.8

^aRelative percent difference (RPD). Relative standard deviation (RSD) is reported for samples 32 and 33 ($n = 3$).

Table S2. SSA results (laboratory 2) for MWCNTs and SWCNTs prepared at 200 °C and 300 °C.

sample	material	BET SSA, m ² /g 200 °C	BET SSA, m ² /g 300 °C	method	RPD
2	MWCNT	77.6	82.6	5-point BET	6.2
5	SWCNT	554.5	557.0	5-point BET	0.4

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Table S3. Results for 5-point BET and 50-point isotherm (laboratory 2).

sample	material	5-point BET	50-point isotherm	RPD
12	SWCNT	440.8	440.8	0
15	MWCNT	80.3	80.0	0.4

Table S4. BET results (laboratory 2) for CNTs and carbon black prepared at 100 °C and 200 °C.

Sample ^a	Material	Metal Mass (%)	5 Point BET Surface Area (m ² /g) Preparation: 30 minutes at 90 °C, 90 minutes at 100 °C	5 Point BET Surface Area (m ² /g) Preparation: Additional 90 minutes at 200 °C
1	Nanoamor, SWCNT	1.85	664.3	680.3
6	Timesnano, SWCNT	0.65	176.1	177.2
7	Mitsui, MWCNT	0.48	21.2	24.0
12	Timesnano, DWCNT	2.98	394.2	396.9
13	Timesnano, MWCNT	7.34	116.1	121.3
22	ASTM carbon black	0.12	140.9	142.9

^aSample numbers correspond to those in Table S5)

Measured and Supplier-listed Surface Areas

For quick reference, an abbreviated version of Table 1 (in paper) is provided below (Table S5) and the corresponding results are plotted in Figure S1. See manuscript for discussion.

Table S5. Sample type, and measured and supplier-listed BET specific surface areas (SSAs). NA indicates SSA was not provided by supplier.

Sample number	Manufacturer, Product	Measured BET SSA, m ² /g	Supplier listed SSA, m ² /g	Purity
1	Nanoamor, SWCNT	662	~400	>90vol% SWCNTs, >95vol%CNTs

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2	Timesnano, SWCNT	367	>380	>90%
3	CNI, SWCNT	144	NA	>90%
4	SWeNT, SWCNT	616	NA	>90% by weight carbon content
5	Nanoamor, MWCNT	146	200–350 ^a	>95%
6	Timesnano, MWCNT	177	>200	>95%
7	Mitsui, MWCNT	22	NA	>95%
8	Timesnano, SWCNT	392	>407	>60%
9	Timesnano, SWCNT	344	>380	>90%
10	Timesnano, SWCNT-COOH (2.73 wt%)	354	>380	>90%
11	Timesnano, SWCNT-OH	310	>380	>90%
12	Timesnano, DWCNT	384	>350	>60%
13	Timesnano, MWCNT	119	>200	>85%
14	Timesnano, MWCNT	74	>100	>99.9%
15	Timesnano, MWCNT	118	>110	>95%
16	Timesnano, MWCNT	180	>200	>95%
17	Timesnano, MWCNT-COOH (2.00 wt%)	171	>200	>95%
18	Timesnano, MWCNT-OH	192	>200	>95%
19	CNF Reactor 1	2	NA	NA
20	CNF Reactor 2	19	NA	NA
21	CNF Final product	35	20–30 ^a	>99% fibrous material
22	SRB 8 ASTM black carbon	141	143	99% carbon by weight

^aFor these two samples, the middle of the supplier-listed range is plotted below in Figure S1 (i.e., sample 5 = 275 m²/g and sample 21 = 25 m²/g).

Figure S1. Measured vs. supplier-listed specific surface areas (SSAs) of CNTs and CNFs. Green points correspond to lowest purity (>60%) CNTs and red point to highest purity (>99%) CNT. Black point is

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ASTM carbon black. Marker number corresponds to sample number in Table S5. Solid line is expected trend (unity slope).

