Conductivity and Ambient Stability of Halogen-Doped Carbon Nanotube Fibers

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Abstract

CNT fibers were fabricated using a variety of spinning conditions and post-spinning processing with the goal of creating a high conductivity yet environmentally stable fiber. These fiber variants were then doped with Br_2, I_2, ICl, or IBr under a variety of conditions with the goal of improving further on the electrical conductivity and stability of fibers. Since high and stable electrical conductivity was the goal, the conductivity of the fibers was monitored over a period of time exceeding 30 days. Additionally, the fibers were imaged with a field emission scanning electron microscope and energy dispersive x-ray spectra and Raman spectra of the fibers were measured for structural changes. Conditions were found where the conductivity of the undoped fiber was both high (over 30,000 S/cm) and stable. Doping with the mixed halogens ICl and IBr improved the conductivity of the fibers more than that of Br_2 or I_2. Although I_2 doped fiber attained their residue compound in the shortest time, both ICl and IBr ultimately had more conductive residue compounds (nearly 60,000 S/cm). It is suspected that more improvements can still be made.

Fibers Used in This Study

RU-n
nth spinning condition of Rice University fibers

T-n
nth spinning condition of scaled-up Rice University fibers

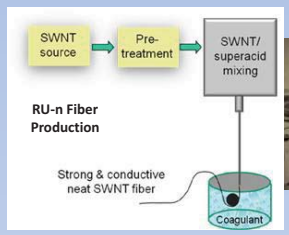
NB-87
Nanocomp fiber

NB-106
Nanocomp fiber

Best Fiber Conductivity, kS/cm

Dopant	As Received	Annealed 155 °C	Br_2	IBr	I_2	ICl
RU-1	14		14	22		
RU-2	10		11	20		
RU-3	3		7	11		10
RU-4	15	15	26	35	31	33
RU-5	16	14	21	32	28	31
RU-6	20		15	28		
RU-7	13		12	25	29	
RU-8	5			33		
RU-9	4			29		
RU-10	24			40		
RU-11	4					
RU-12	29			41		42
RU-13	35		58	55	54	58
T-1	5	6	10	12	10	13
T-2	32	27	54	44		43
NB-87	4		17	19	14	14
NB-106	18		40	38	33	38

Best Value | Still Changing

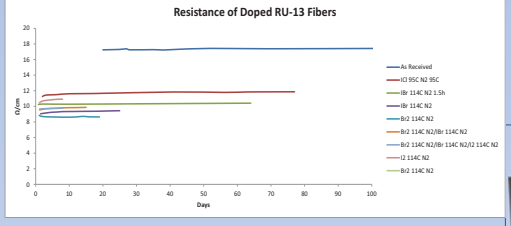


Spinning CNT fibers from $HOSO_2Cl$ solution
Behabtu et al, Science **339** (2013) p. 182.

Vapor-Phase Halogenation Reactions
Br_2, ICl, IBr, I_2

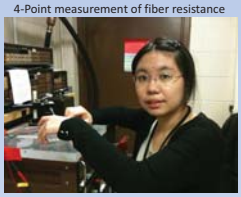
	-7.2 °C	20 °C	60 °C	95 °C	114 °C	155 °C	187 °C
As Received						x	
Br_2	x	x	x	x	x		
ICl				x	x		
IBr					x		
I_2				x	x		x

Long Term Stability of Halogen-Doped Fibers is Excellent



Fibers mounted on 4-point resistance plates w/silver paint

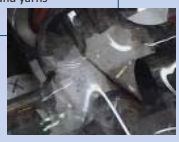
4-Point measurement of fiber resistance



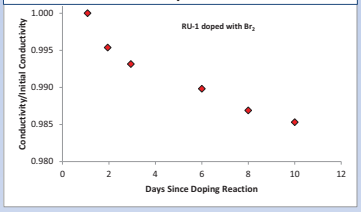
NB-n Fiber Production

"(Nanocomp Technology Inc.) production systems generate a "cotton candy" or "stocking-like" flow of millimeter-length CNTs that can be translated into multiple formats, each of which possess a different mix of strength and conductivity", including lightweight wires and yarns

http://www.nanocomptech.com/conductors-and-yarns



Short Term Conductivity Decreases as Residue Compound is Formed

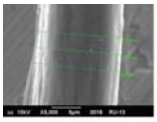


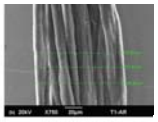
Single-slit-like fiber diameter measurement

Field Emission Scanning Electron Microscopy

RU-13 As Received

Relatively smooth
15 µm diameter



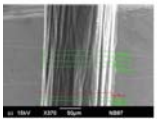


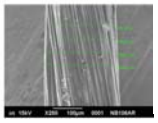
T1 As Received

Multi-filament
100 µm diameter

NB-87 As Received

Deep Striations
160 µm diameter

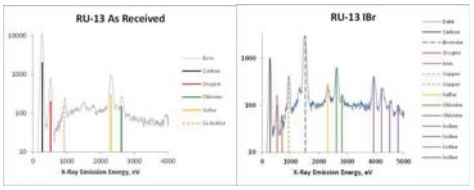




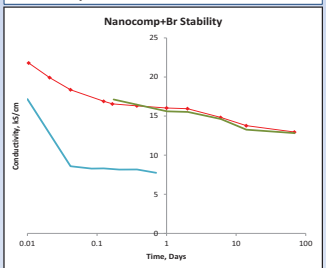
NB-106 As Received

Striations
250 µm diameter

Energy Dispersive X-Ray Spectroscopy confirms dopants in fibers

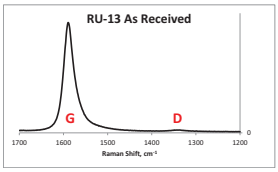


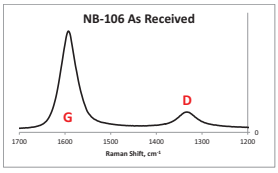
Heating Br_2-doped fibers to 100 °C has no effect, but heating to 200 °C significantly degrades conductivity.



Resistivity of fibers stored under ambient lab conditions, heated to 100 °C for 1 hour and then stored under lab conditions, heated to 200 °C.

Raman Spectroscopy





Raman D/G ratios show doping does not dramatically increase disorder in fibers

	As Received	Annealed 155 °C	Br_2	IBr	I_2	ICl
RU-4	0.032	0.027	0.032	0.022	0.043	0.039
RU-5	0.026	0.022	0.020		0.024	
RU-12	0.016			0.028		0.017
RU-13	0.019			0.017		0.018
T-1	0.015	0.023	0.026	0.026	0.026	0.022
T-2	0.049		0.040	0.025		0.031
NB-87	0.27		0.34	0.25	0.30	0.24
NB-106	0.27		0.28	0.24		0.41

Acknowledgements

NB-87 and NB-106 fibers kindly provided by Nanocomp Technologies (Merrimack, NH). Research supported by the NASA Glenn Center Innovation Fund, and Teijin Aramid.