Electronic Supplementary Material (ESI) for ChemComm.

High Yield Photolysis of Brominated Single-walled Carbon Nanotubes and their Application for Gas Sensing

D. Hines,[a] M. H. Rümmeli,[b,c] D. Adebimpe*[,d] and D. L. Akins[a,*]

[a] Department of Chemistry and CASI, The City College of New York and the Graduate School and University Center (CUNY), New York City, NY, USA

[b] IBS Center for Integrated Nanostructure Physics, Institute for Basic Science (IBS), Daejon 305-701, Republic of Korea

[c] Department of Energy Science, Department of Physics, Sungkyunkwan University, Suwon 440-746, Republic of Korea

[d] Polymath Interscience LLC, Annapolis, MD, USA

* akins@sci.ccny.cuny.edu, david@polymath.com

Supporting Information

Materials and Methods

The N-bromosuccinamide (99 %) was purchased from Sigma Aldrich. Dichloromethane (ACS: 99.5% stab. with amylene), chloroform (HPLC grade: 99.5% min) and di-ethyl ether (99+ %) were purchased from Alfa Aesar. Single-walled carbon nanotubes (purity: 95 wt.%) were purchased from UnidymTM Inc., Sunnyvale, CA, and used without further purification. The individual SWNTs diameters ranged from ca. 0.8 to 1.2 nm; with individual lengths of ca.100 to 1000 nm. The nanotubes are bundled as ropes; maximum density of 1.6 g/cm^3. The moisture content for SWNTs dry powder was <5 wt.%.

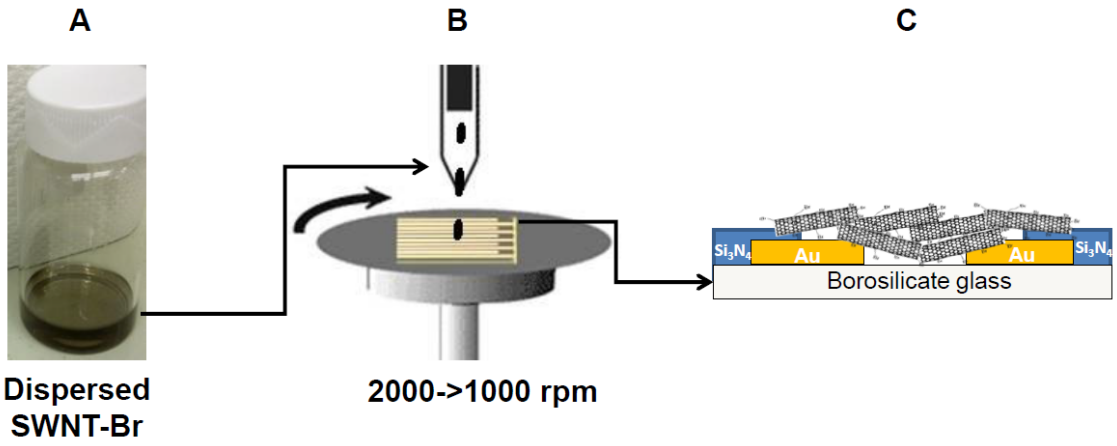

Figure S1. Schematic illustration of **(a)** dispersed Br-SWNT, **(b)** spin casting onto interdigitated Au electrodes (IDE), and **(c)** IDE decorated with Br-SWNT.

The experimental setup for the sensor is provided in Figure S2 (of the SI document). It consists of two main subsystems: (a) The vapor delivery and distribution sys-tem, which allows one to initially purge the sensor environmental chamber with an inert gas and then to deliver selected quantities of analyte vapor and carrier gas (N2, 0.025 l/min.) to the sensing chamber; (b) the response monitoring and data acquisition subsystem, which detects variations in the resistance of the brominated-SWNT mat that changes due to vapor molecule adsorption.

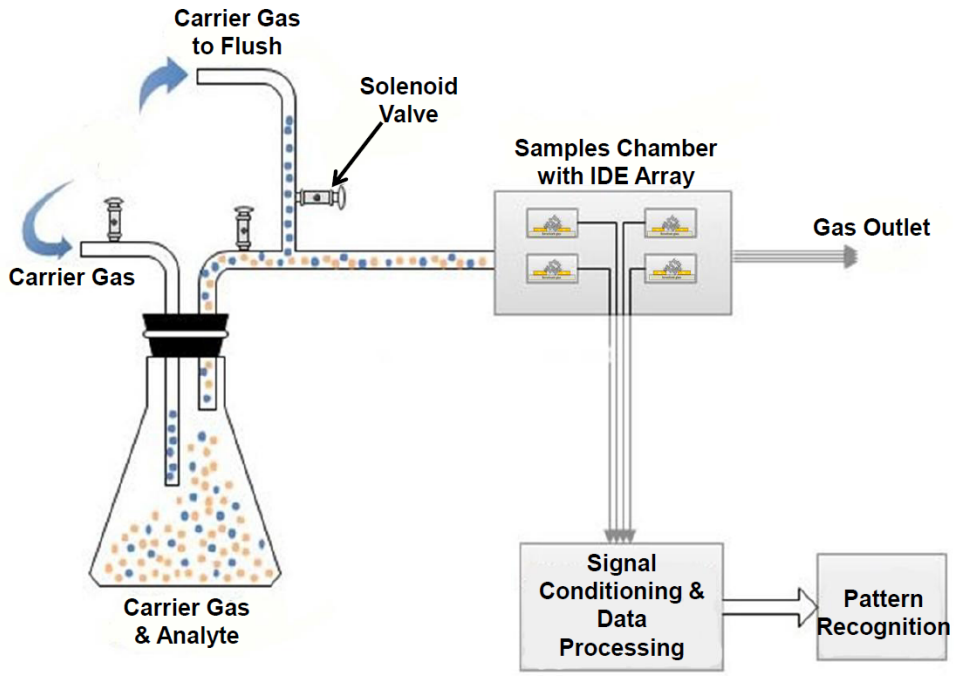

Figure S2. Diagram of the vapor delivery, distribution and data acquisition subsystems.

Characterization Techniques

Raman spectra were collected using a HR800 Horiba Jobin Yvon Raman Microprobe spectrometer. Solid samples were placed on a cover glass and excited with a 632.8 nm HeNe laser radiation (x100 objective lens). Low volt-age scanning transmission electron microscopy (SEM) measurements were accomplished using a Zeiss Supra 55VP Scanning Electron Microscope coupled with a Genesis EDX system. For surface topographical imaging of the SWNT mats created for the gas sensing electrodes, a TopoMetrix Explorer AFM was used in the contact mode. Fourier-transform infrared (FTIR) measurements were conducted using a Varian 7000 FTIR. For the FTIR investigations, the SWNT samples (ca. 1 mg) were mixed with KBr and pressed into pellets using standard procedures. Thermogravimetric investigations were accomplished on a TA Instruments Thermogravimetric Analyzer / Differential Scanning Calorimeter (Q600). For this latter system, ca. 12 mg of SWNT samples, pristine or Br-SWNT, were loaded into the sample cell with the reference cell left empty. The sample and reference cells were maintained at 25 oC for 5 minutes, after which they were heated at a rate of 100 oC/min in a nitrogen atmosphere, with a flow rate of 100 mL/min.

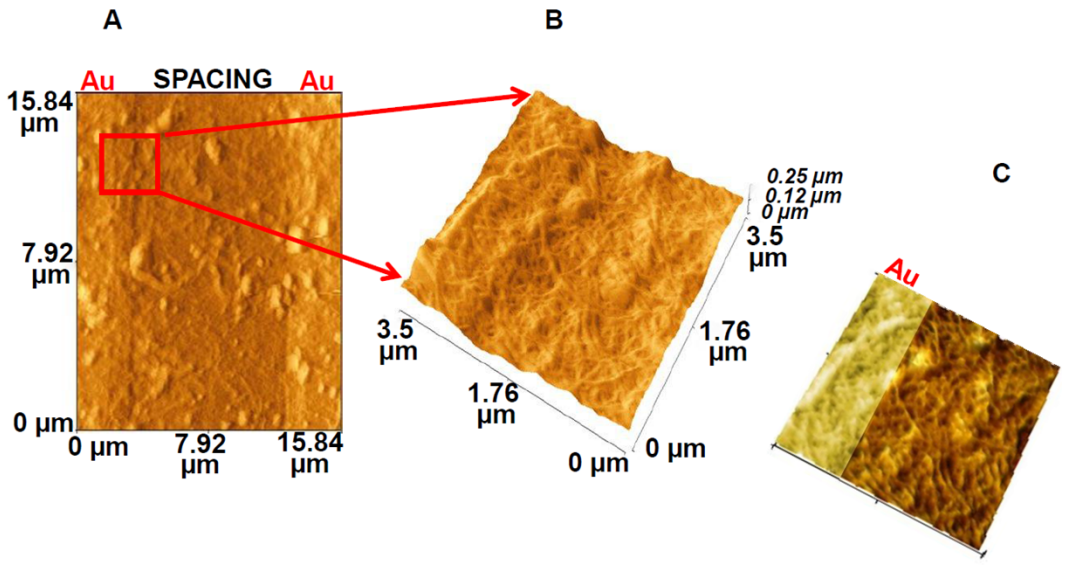

Figure S3. AFM images: **(A)** Br-SWNT mat bridging adjacent electrodes (acquired at scan rate: 32 µm/s). **(B)** 3D image showing scan of highlighted region in (A); note the presence of Br-SWNTs on electrode as well as in the channel between electrodes. **(C)** Highlighted Au electrode using semitransparent color.

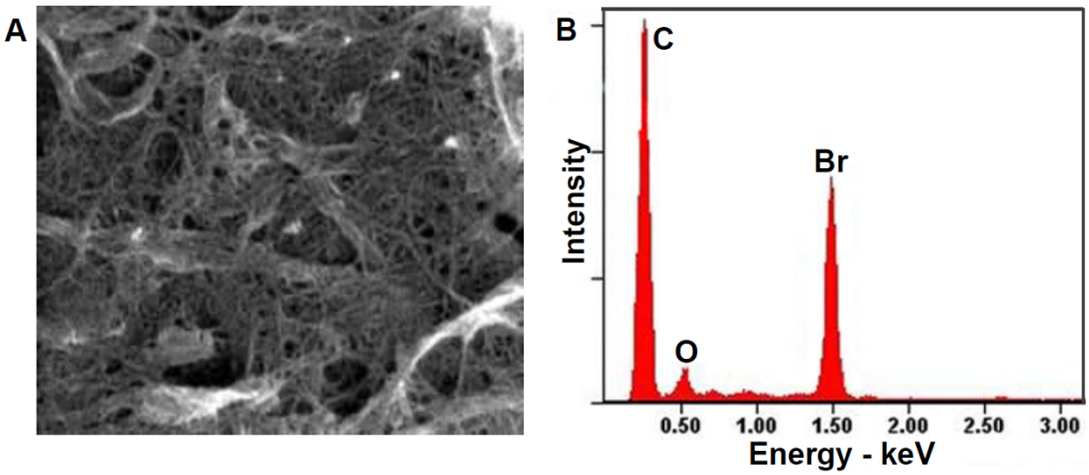

Figure S4. **(A)** SEM surface and **(B)** elemental analysis of Br-SWNT sample.

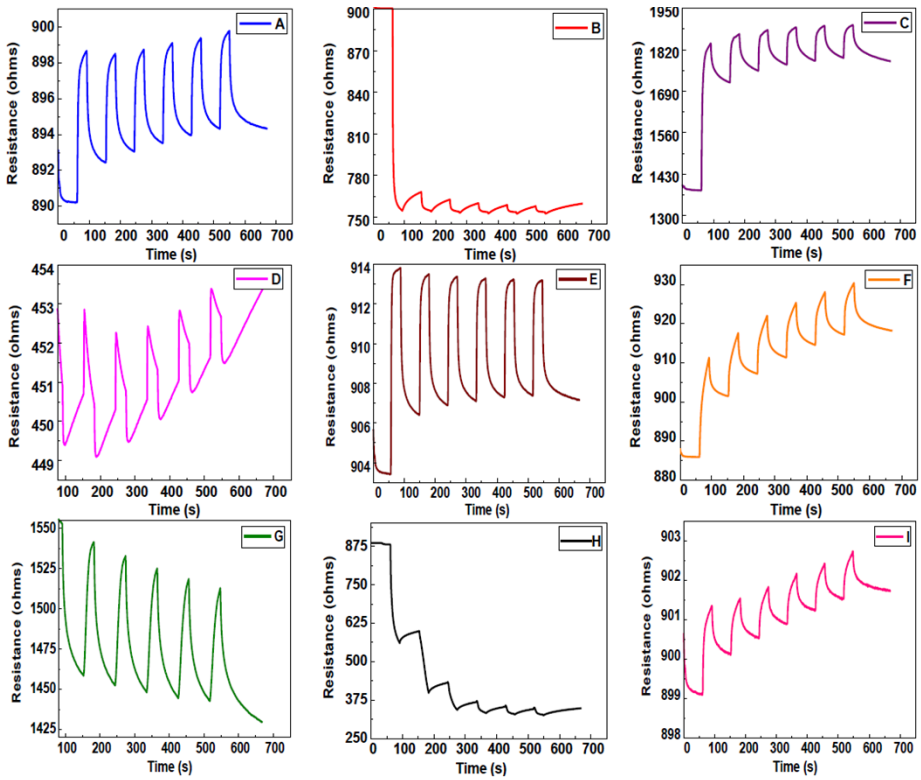

Figure S5. Sensor response data of the gas sensor using Br-SWNT as sensing agent for (A) ethanol, (B) HCl, (C) ammonia, (D) sulfuric acid, (E) acetonitrile, (F) N,N-dimethylacetamide, (G) acetic acid, (H) nitric acid, and (I) 2-proponal.

Table S1: EDX elemental data for different Br-SWNT samples and synthesis times

Wt.%	At.%	Synthesis Time (hrs.)	Br-SWNT Samples (†)
12.80	2.21	48	C
14.47	2.54	48	C
18.27	3.36	48	C
19.85	3.68	24	B
16.95	3.22	24	B
15.81	2.87	24	B
7.52	1.24	12	A

† Sample A was brominated for 12 hours; 3 different representative samples B were each brominated for 24 hrs.; 3 different representative samples C were each brominated for 48 hrs.

Tables S2. Concentration of Analytes Exposed to Br-SWNT Gas Sensor Element

analytes	concentration (ppb)	Density - g/m^3@ 20^oC	molecular wt. (g/mol)
Ethanol	608	7.89×10^5	46.07
HCl	769	1.18×10^6	36.46
Acetonitrile	683	7.83×10^5	41.05
N,N-dimethylacetamide	322	9.37×10^5	87.12
Ammonia	1645	5.988×10^3	17.03
Acetic Acid	467	1.049×10^6	60.05
Nitric Acid	445	1.413×10^6	63.01
Sulfuric Acid	286	1.284×10^6	98.08