

Fully-Drawn Carbon-Based Chemical Sensors on Organic and Inorganic Surfaces

Kelvin M. Frazier, Katherine A. Mirica, Joseph J. Walish, Timothy M. Swager*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA
02139 (USA)

[*] **Corresponding author:** tswager@mit.edu

Sensing data acquisition was done using PSTrace software provided by Palm Instruments. Matlab (R2012a, Mathworks) and Microsoft Excel (2010) were used to calculate normalized sensing responses and principal component analysis.

Chemical-Etching Procedure:

A thick layer of etching cream (Cat. No. 15-0200, Armour Products) was applied to cover the desired surface of the glass and allowed to remain for 5 min. All traces of the Armour Etch Cream were washed with tap water and dried using a stream of nitrogen.

Profilometry:

Surface roughness of weighing paper, glass, PMMA, alumina, adhesive tape, and silicon wafer was measured using a Dektak 6M Stylus Profiler (Veeco Inc.) with a stylus radius of 2.5 μm over a distance of 1400 μm with duration of scan of 30 s and applied force corresponding to a mass of 1 mg. The average measurement of surface roughness and the standard deviation were calculated from four scans over different regions between four gold electrode gaps of the same substrate.

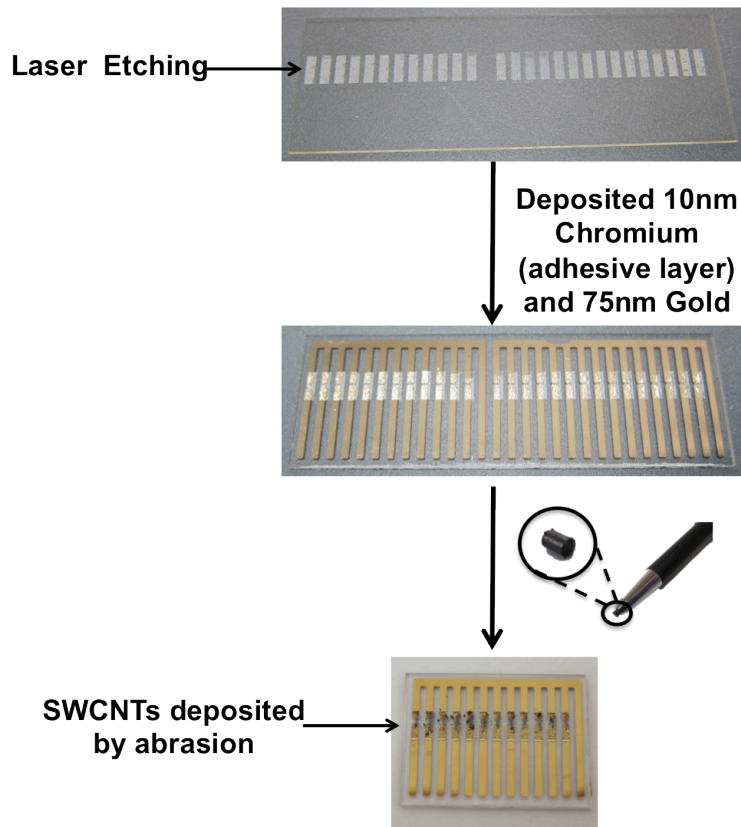


Figure S1. A stepwise procedure for the fabrication of partially-drawn SWCNT-based chemiresistive sensors on laser-etched glass. Step 1 involves laser etching of glass to define regions onto which the sensing material will be deposited. Step 2 involves deposition of gold electrodes on the surface of glass by thermal evaporation. Step 3 involves bridging the gap between the gold electrodes by depositing a film of SWCNTs by mechanical abrasion into etched regions of glass.

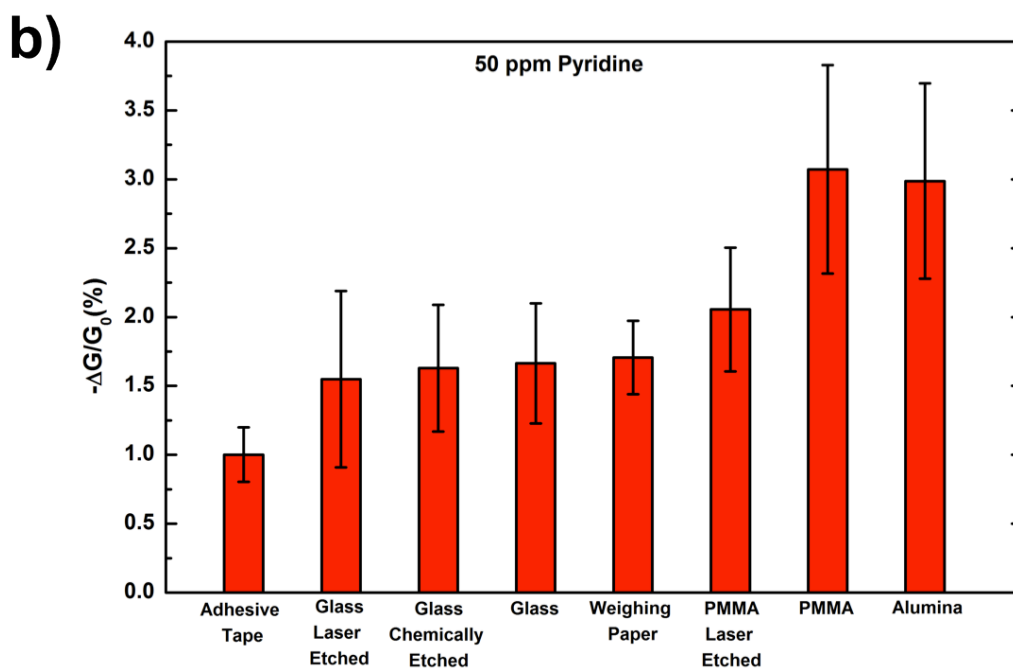
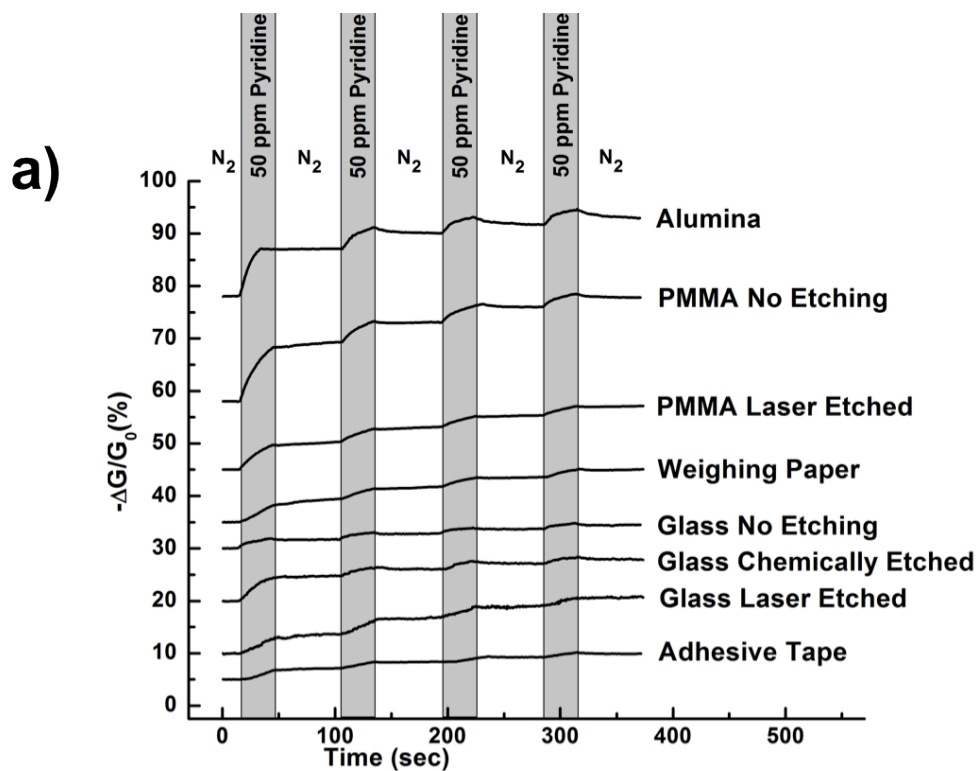


Figure S2. Sensing response of Pristine SWCNTs devices deposited by abrasion onto various substrates using gold electrodes (0.3 mm gap size). a) Normalized change of conductance over time from devices simultaneously exposed four consecutive times to 50 ppm pyridine for 30 s with recovery time of 60 s. b) Normalized average conductive responses (first exposure exempt) of at least three sensors simultaneously exposed four consecutive times to 50 ppm pyridine for 30 s with recovery time of 60 s.

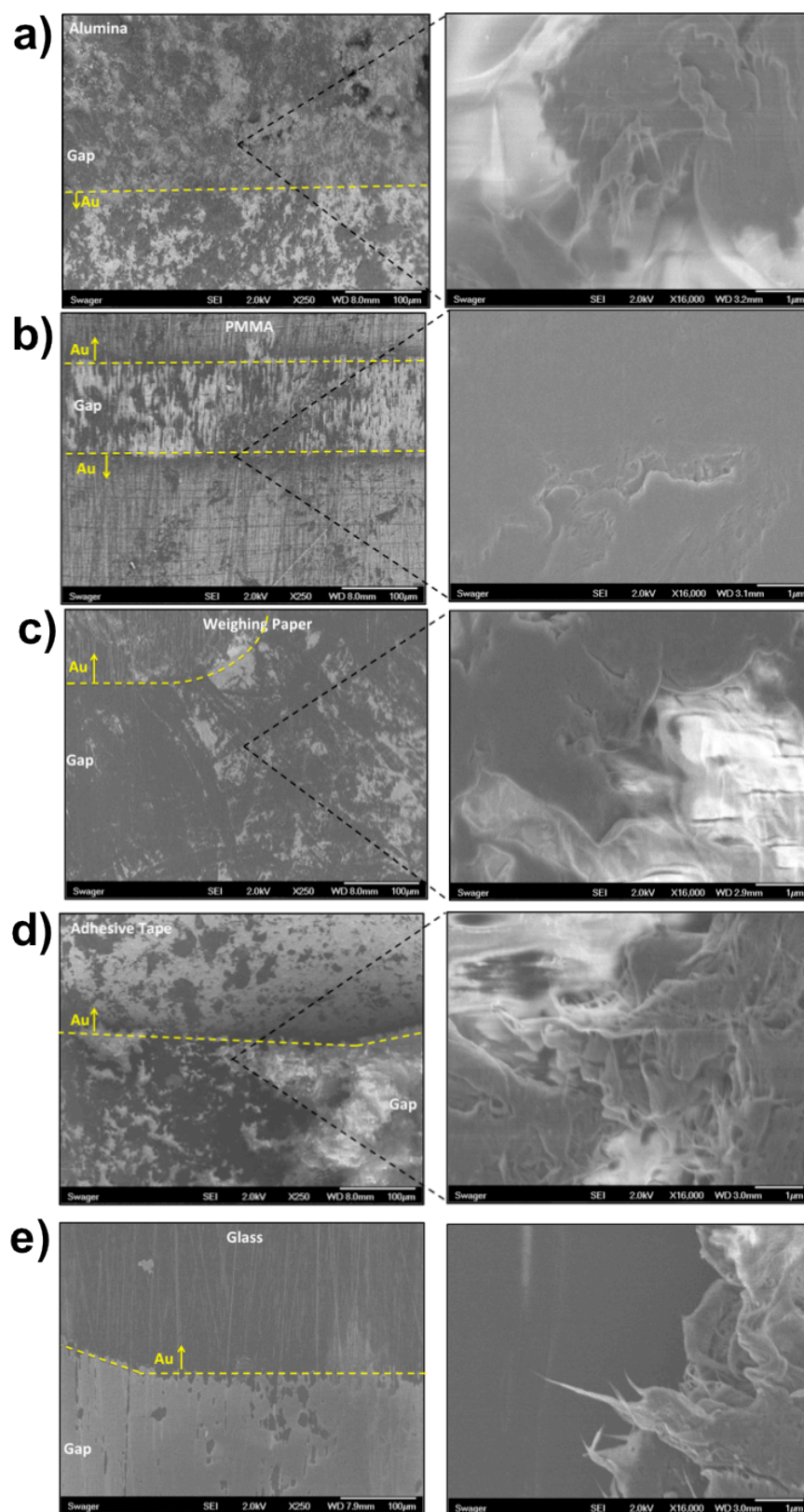


Figure S3. Characterization of abraded films of sensing materials using high resolution Scanning Electron Microscopy (SEM). a-e) Images of compressed pristine SWCNTs deposited by abrasion between and on top of gold electrodes onto alumina, PMMA, weighing paper, adhesive tape, and glass, respectively.

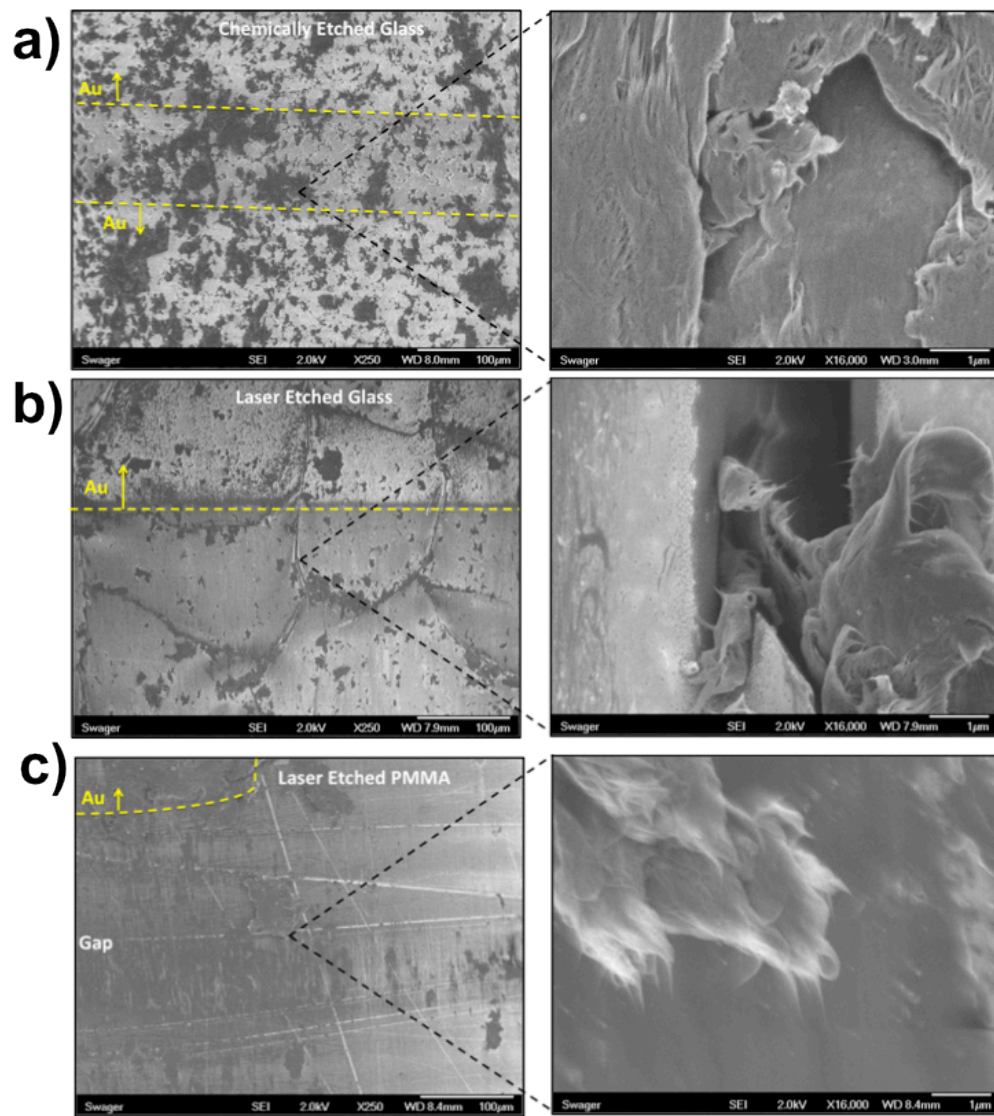


Figure S4. Characterization of abraded films of sensing materials using high resolution Scanning Electron Microscopy (SEM). a-c) Images of compressed pristine SWCNTs deposited by abrasion between and on top of gold electrodes onto chemically etched glass, and laser etched glass/PMMA.

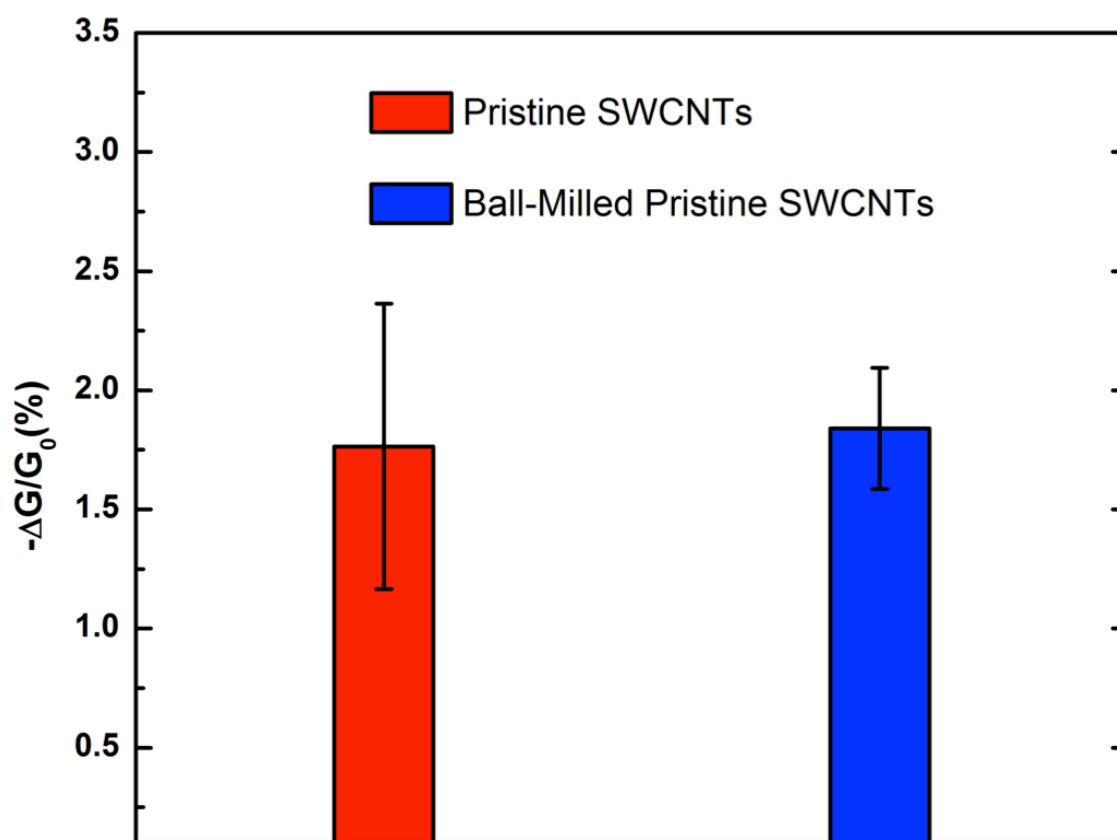


Figure S5. Investigation of the effect of ball milling on performance of SWCNTs as chemical sensing materials. Normalized average conductive responses of three pristine SWCNT-based sensors on weighing paper with gold electrodes simultaneously exposed four consecutive times to 50 ppm pyridine (first exposure exempt) for 30 s with recovery time of 60 s.

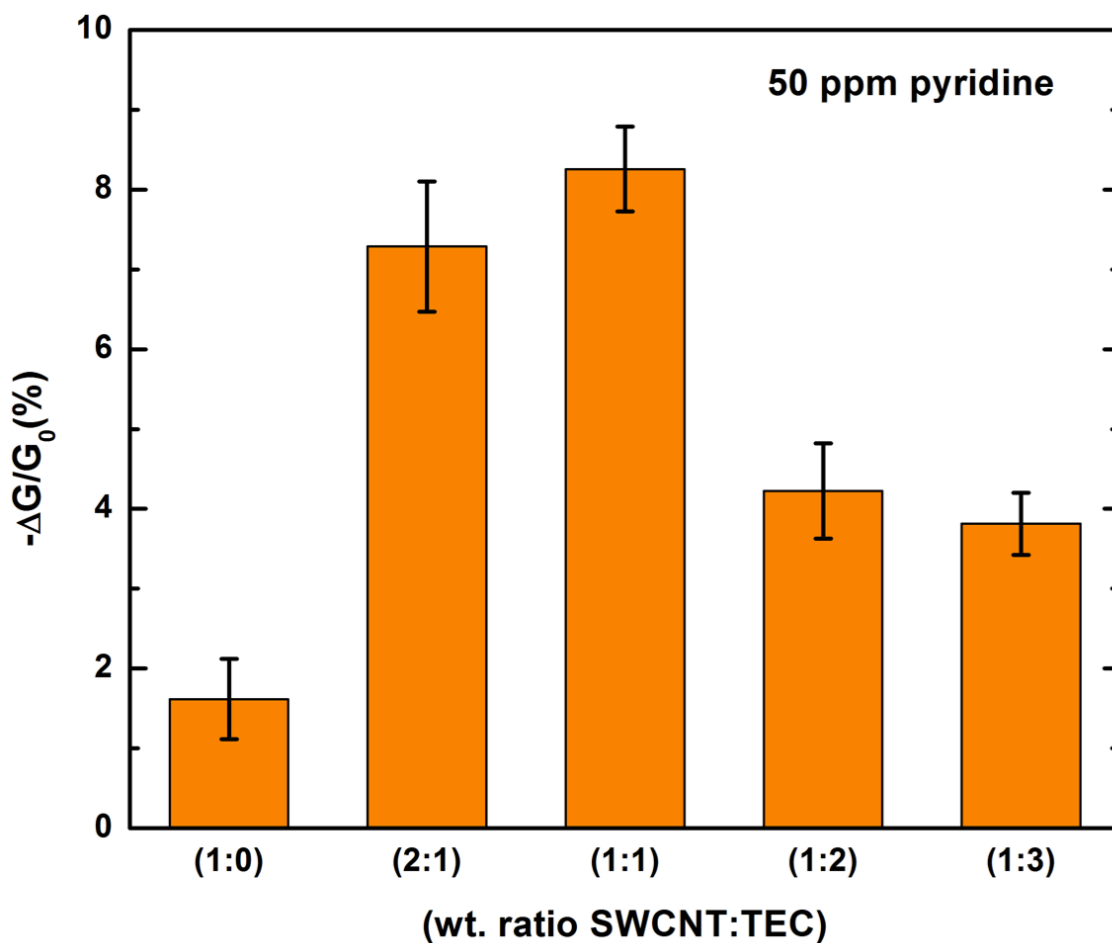


Figure S6. SWCNT and TEC was mechanically mixed at different mass ratios, compressed, and deposited between and on top of gold electrodes onto weighing paper (0.3 mm gap size). Normalized average conductive responses of two sensors simultaneously exposed four consecutive times to 50 ppm pyridine (first exposure exempt) for 30 s with a recovery time of 60 s.

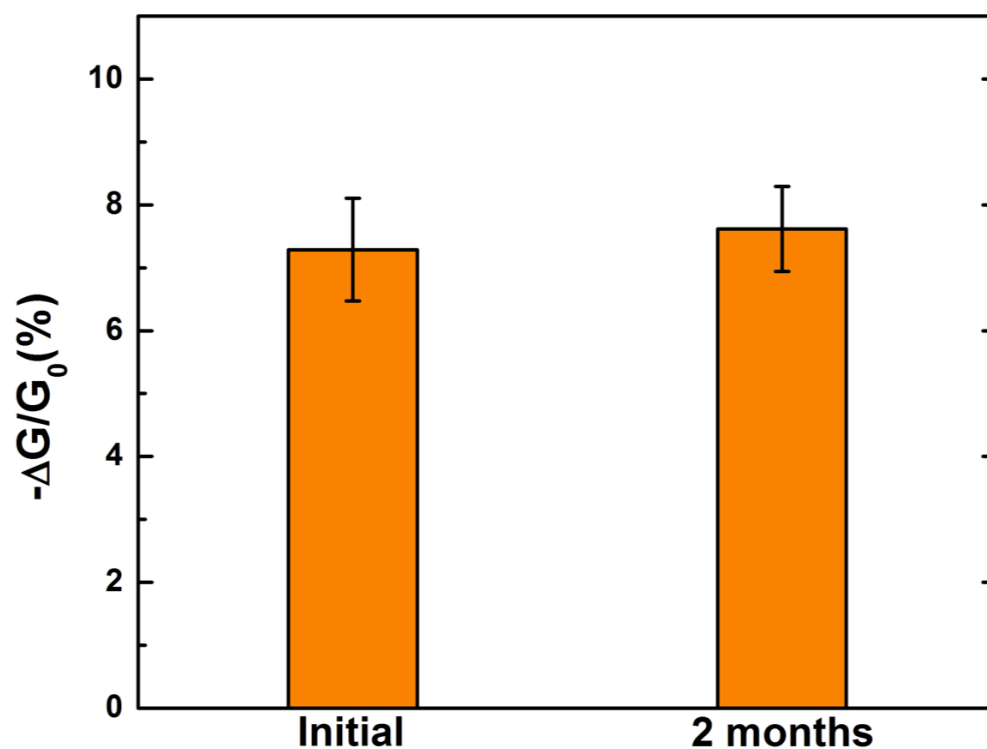


Figure S7. Stability of PENCILs. SWCNT and TEC (2:1 mass ratio) was mechanically mixed and deposited between and on top of gold electrodes onto weighing paper. Normalized average conductive responses of at least two sensors simultaneously exposed at least four consecutive times to 50 ppm pyridine (first exposure exempt) for 30 s with a recovery time of 60 s.

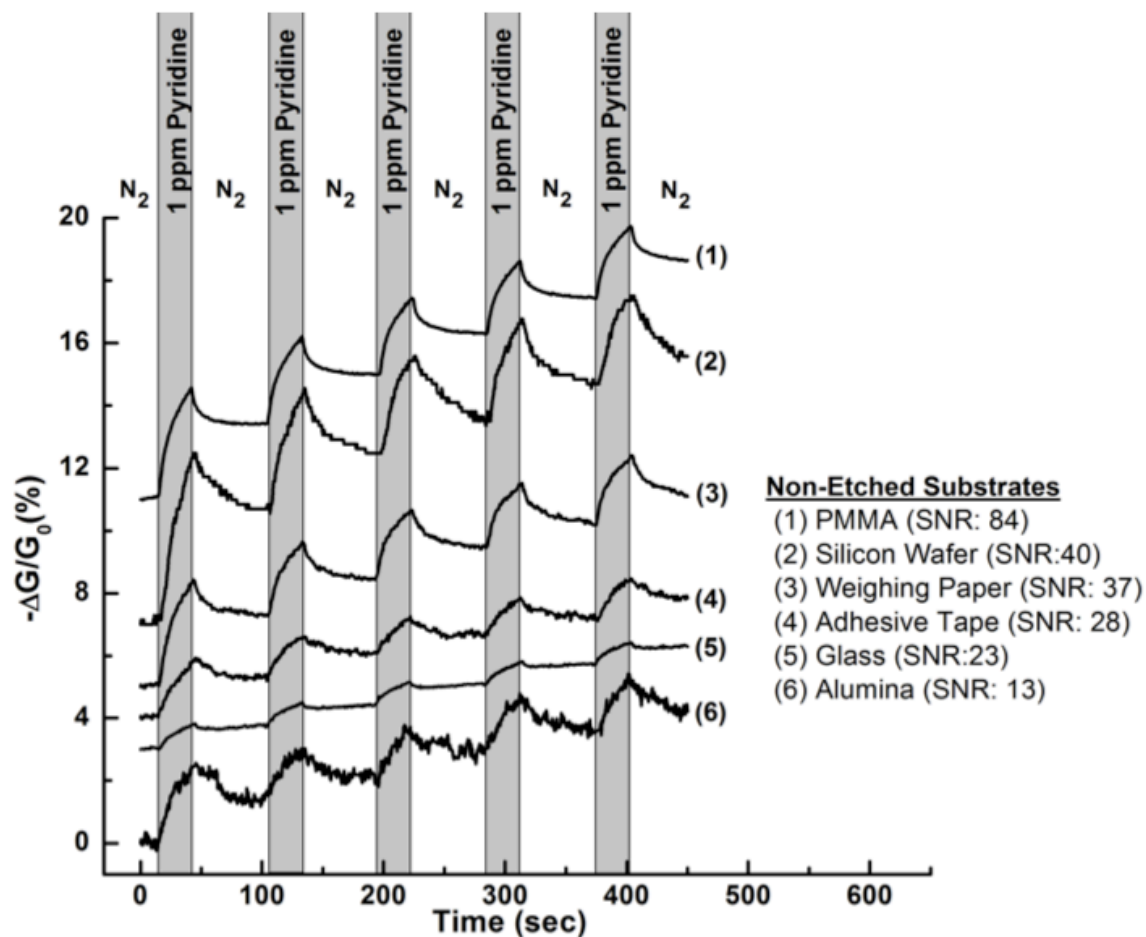


Figure S8. Investigation of the SWCNT-based chemiresistor's sensitivity on various unmodified substrates. Normalized change of conductance over time from devices simultaneously exposed five consecutive times to 1 ppm pyridine for 30 s with a recovery time of 60s. Devices were fabricated by depositing SWCNT:TEC (2:1 mass ratio) on top of and between gold electrodes by abrasion onto various substrates.

Glass						Adhesive Tape					
Device -ΔG/G ₀ (%)	Exposure (50 ppm Pyridine)					Device -ΔG/G ₀ (%)	Exposure (50 ppm Pyridine)				
	1	2	3	4	5		1	2	3	4	5
1	2.681994599	2.50515168	2.328322819	2.32832282	2.21043457	1	6.74361725	5.83232526	4.52612896	4.31348595	3.9489706
2	2.48011096	2.33972627	2.10575922	2.05896804	2.01216571	2	9.30611923	6.24490259	5.67347652	5.55101695	5.46939022
3	2.809538145	2.61352241	2.482847844	2.41750667	2.31950659	3	10.4514714	6.68325454	6.54105944	6.25666076	5.9367239
4	3.206706066	2.86137555	2.713372552	2.68869558	2.59003476	4	13.2349655	7.81765585	7.13499436	6.78264838	6.91477353
5	2.845763745	2.5042702	2.333523421	2.30506789	2.27660557	5	14.4788349	8.57346731	8.00426524	7.57737641	7.61294836
6	3.264977026	2.96816327	2.806262521	2.80626252	2.64436177	6	11.8547745	7.4803203	6.95538746	6.7366598	6.60542007
7	2.883278345	2.66149024	2.578324665	2.49514587	2.35652996	7	11.6038209	7.4595963	6.96228659	6.46497688	6.54786512
8	4.64862109	3.91031237	3.718892961	3.69155012	3.52748007	8	10.9140538	7.0668499	6.35743594	6.27557999	6.05730177
Average Response	3.1	2.8	2.6	2.6	2.5	Average Response	11	7.1	7	6	6
Standard Deviation	0.7	0.5	0.5	0.5	0.5	Standard Deviation	2	0.9	1	1	1
Overall Coefficient of Variance	20%		Overall Coefficient of Variance (first exposure exempt)		18%	Overall Coefficient of Variance	31%	Overall Coefficient of Variance (first exposure exempt)		16%	
Alumina						Weighing Paper					
Device -ΔG/G ₀ (%)	Exposure (50 ppm Pyridine)					Device -ΔG/G ₀ (%)	Exposure (50 ppm Pyridine)				
	1	2	3	4	5		1	2	3	4	5
1	13.59504074	8.01652891	7.314051248	7.1487592	6.81818003	1	10.0404557	7.09820048	6.47297211	6.21551688	6.06840587
2	13.5201551	8.16125839	7.325468881	7.22714174	6.63716716	2	13.3563401	8.67422352	8.03351326	7.88565614	7.78708669
3	12.66029908	7.33970092	6.766715727	6.54843101	6.19372403	3	12.2302064	8.16758636	7.44816364	7.27888948	7.19424232
4	15.05604576	7.39847665	6.9954485	6.93787697	6.79392756	4	12.8393467	8.46375284	7.6333465	7.50559343	7.44171309
5	12.07430556	9.08153325	7.80873729	7.49913761	6.15754719	5	13.5167982	8.37717527	8.45810829	7.85107205	7.72967253
6	14.15999413	8.87999535	8.559999466	7.92000771	8.07999611	6	13.0000045	8.68421436	7.89473519	7.6842116	7.6842116
7						7	11.8730395	8.11128579	7.28839604	7.13165825	7.01410257
8						8					
Average Response	14	8.1	7.5	7.2	6.8	Average Response	12	8.2	7.6	7.4	7.3
Standard Deviation	1	0.7	0.6	0.5	0.7	Standard Deviation	1	0.5	0.6	0.6	0.6
Overall Coefficient of Variance	30%		Overall Coefficient of Variance (first exposure exempt)		11%	Overall Coefficient of Variance	24%	Overall Coefficient of Variance (first exposure exempt)		9%	
PMMA						Silicon					
Device -ΔG/G ₀ (%)	Exposure (50 ppm Pyridine)					Device -ΔG/G ₀ (%)	Exposure (50 ppm Pyridine)				
	1	2	3	4	5		1	2	3	4	5
1	10.13526496	7.12516798	6.267860386	5.8296862	5.31530346	1	10.1851863	6.27572615	5.86420196	5.24691176	5.0411536
2	8.942668887	6.38517343	5.698596694	5.21798643	4.80604531	2	13.4642329	7.85414032	7.29312304	6.73212715	6.45161049
3	9.858612413	6.78257557	5.961029086	5.50248558	4.98661959	3	6.55737705	6.77595295	6.77595295	6.88524924	9.18032954
4	9.498780337	6.60784213	5.838180253	5.38765105	4.82447837	4	13.8345819	8.49623142	7.59398955	7.14286288	6.9924835
5	10.34635383	7.10391051	6.190126105	5.7332339	5.20265508	5	14.0449429	8.42696039	7.44381867	7.30336603	7.02247682
6	10.5536855	7.28187882	6.375840295	5.87248911	5.35235263	6	13.636359	8.55615142	7.62031646	7.08555509	7.21924288
7	12.19365222	8.28446966	7.262062327	6.735828	6.20959368	7	11.2299481	7.21925308	6.68448151	6.41711612	6.14973543
8	10.00481202	7.01782208	6.134574514	5.68492176	5.18708755	8	14.8203609	9.43113044	8.38323087	8.23353256	7.78443763
Average Response	10	7.1	6.2	5.7	5.2	Average Response	12	8	7.2	6.9	7
Standard Deviation	1	0.6	0.5	0.5	0.4	Standard Deviation	3	1	0.8	0.8	1
Overall Coefficient of Variance	27%		Overall Coefficient of Variance (first exposure exempt)		14%	Overall Coefficient of Variance	30%	Overall Coefficient of Variance (first exposure exempt)		14%	

Table S1. Device-to-device variance of chemiresistive material on 6 different substrates. Normalized average conductive response to 50 ppm pyridine 5 consecutive times for 30 s with recovery time of 60 s. Devices were fabricated by depositing SWCNT:TEC (2:1 mass ratio) on top on and between gold electrodes onto glass, adhesive tape, alumina, weighing paper, PMMA, or silicon.

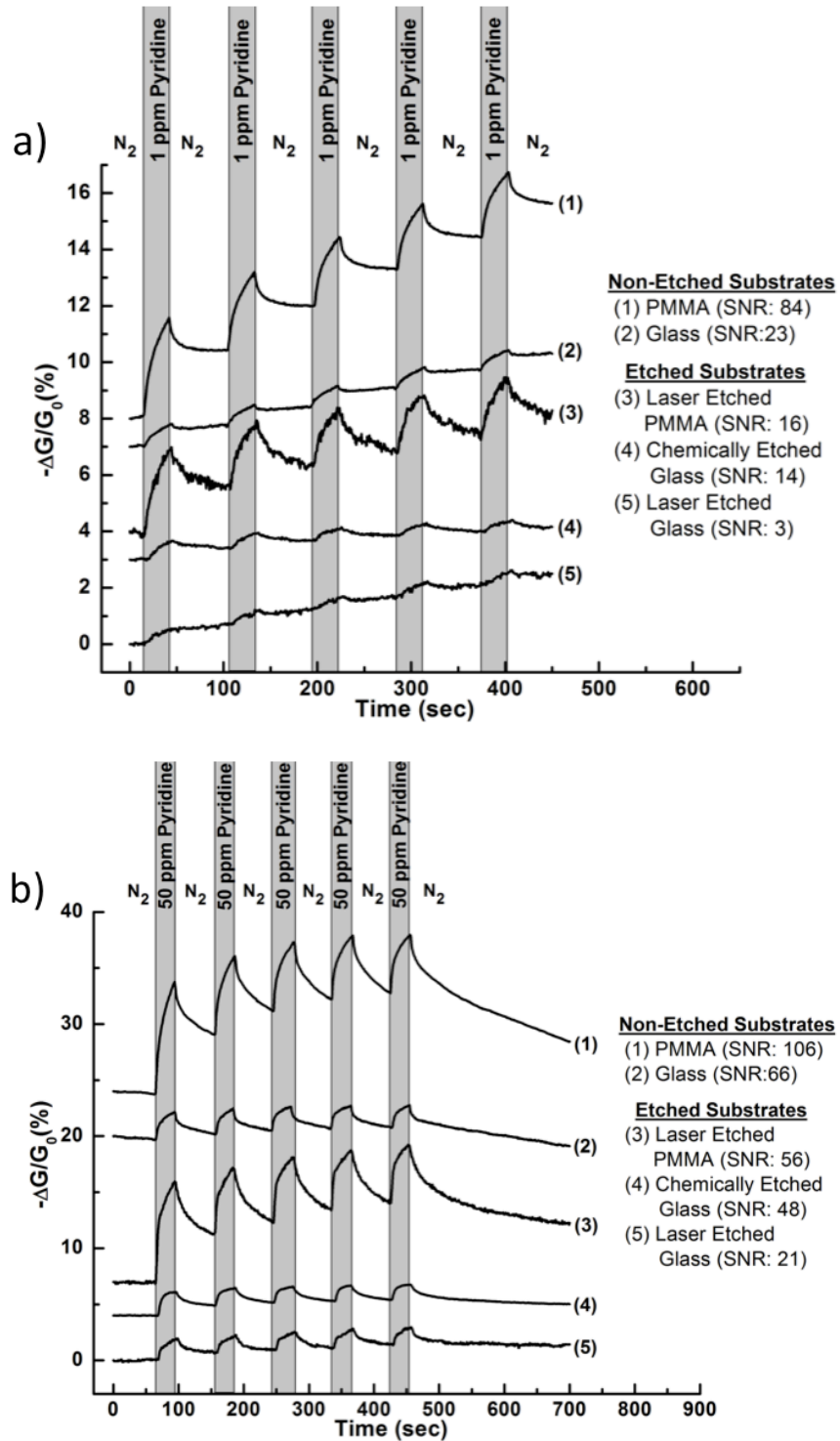


Figure S9. Comparison study of SWCNT-based chemiresistor's sensitivity on various modified or unmodified substrates. Normalized change of conductance over time of devices simultaneously exposed five consecutive times to 1 ppm (a) and 50 ppm (b) pyridine for 30 s with recovery time of 60s. The devices were fabricated by depositing SWCNT:TEC (2:1 mass ratio) on top of and between gold electrodes by abrasion onto various modified and unmodified substrates.

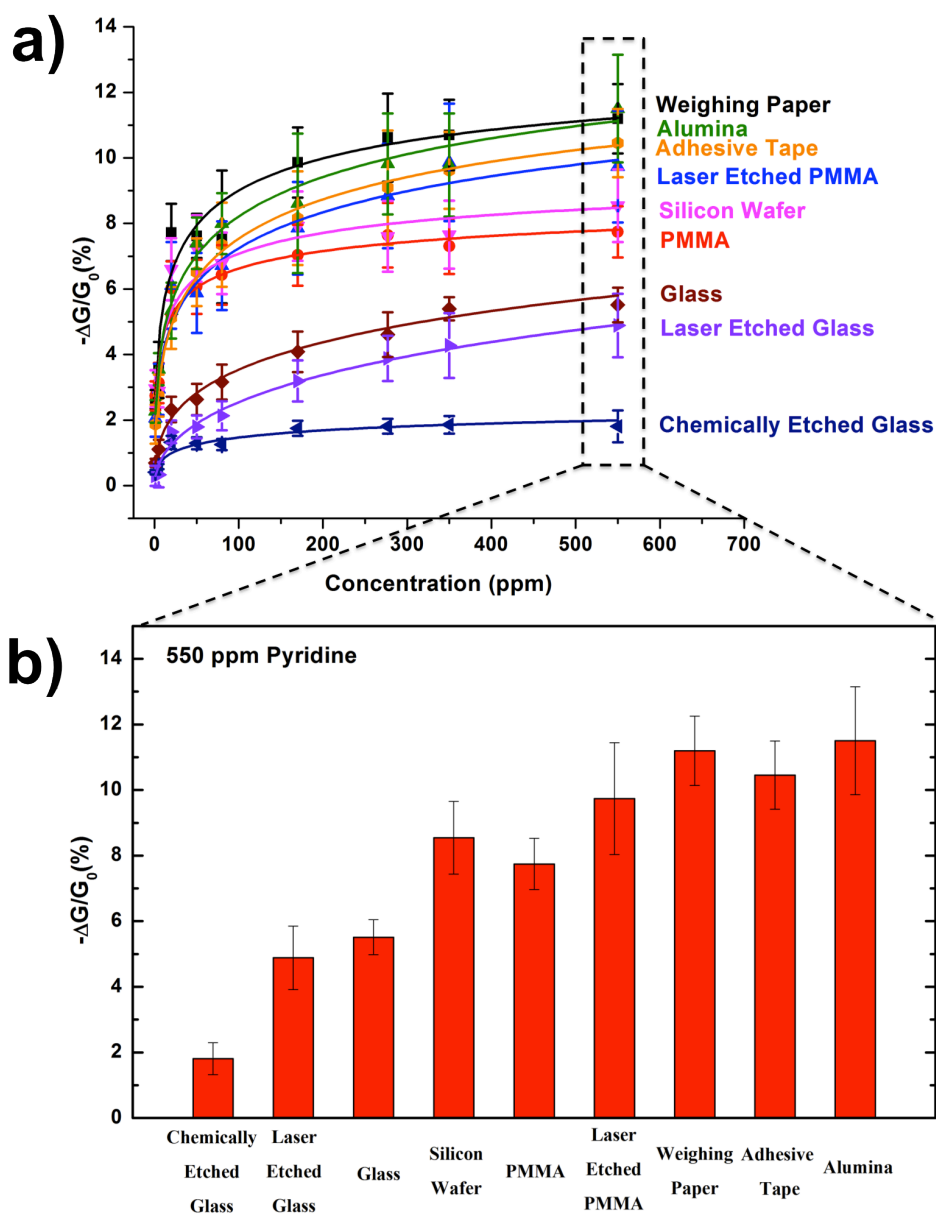


Figure S10. Sensing response of SWCNTs-TEC (2:1 wt. ratio) deposited by abrasion on various substrates between gold electrodes (1 mm gap size). a) Normalized average conductive responses (first exposure exempt) of at least six sensors simultaneously exposed five consecutive times to various concentrations of pyridine for 30 s with recovery time of 60 s. b) Substrate effects on the sensory performance was further investigated by analyzing the normalized average conductive responses (first exposure exempt) upon exposure to 550 ppm pyridine.

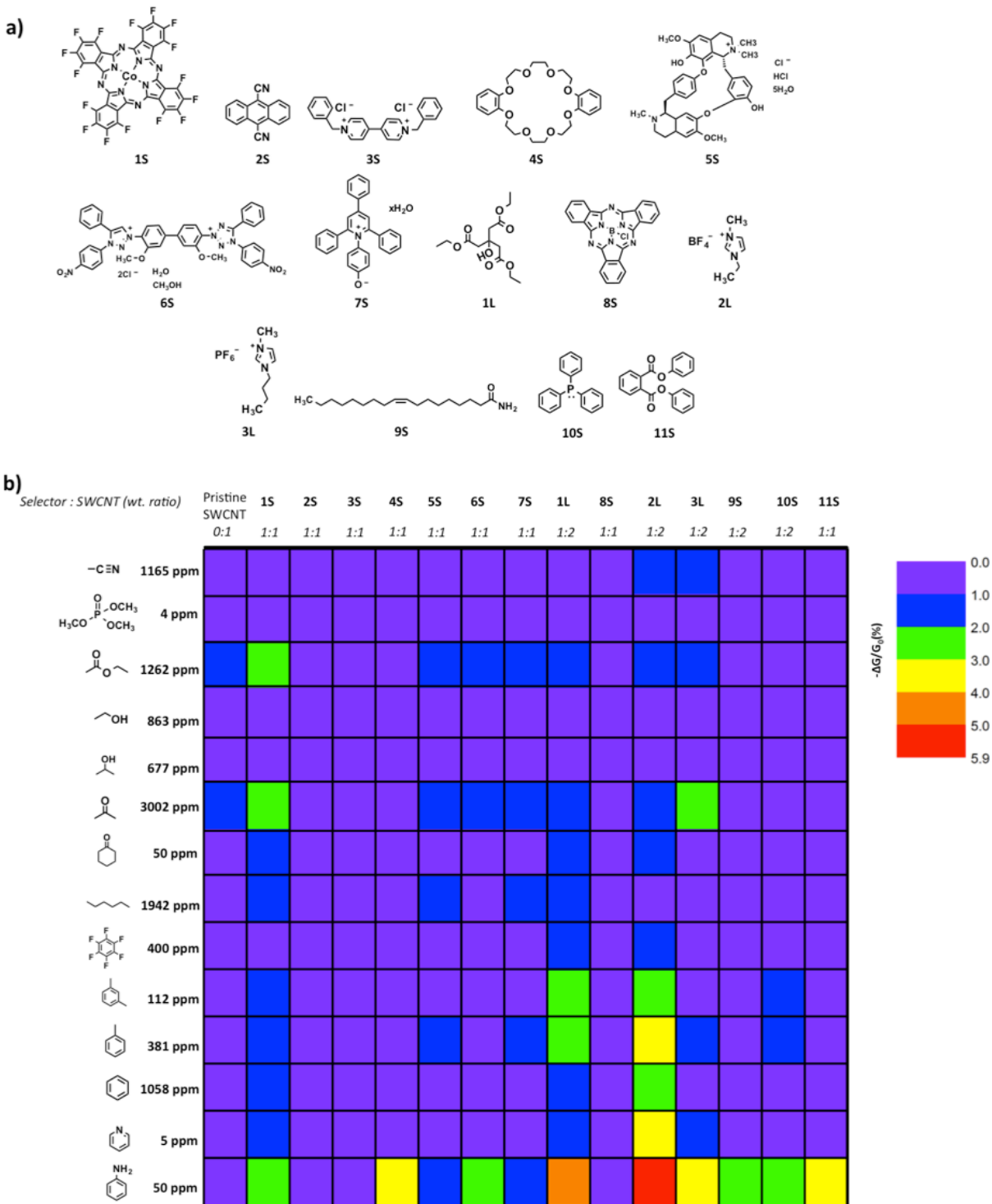


Figure S11. Sensing response of chemiresistor array fabricated on adhesive tape. The devices were fabricated by depositing SWCNT:Selector mixtures on top of and between gold electrodes by abrasion onto adhesive tape. a) Schematic diagram of the chemical structures of selectors used in the array. b) Normalized average conductive response (first exposure exempt) of three devices simultaneously exposed five consecutive times to various VOCs for 30 s with a recovery time of 60s.

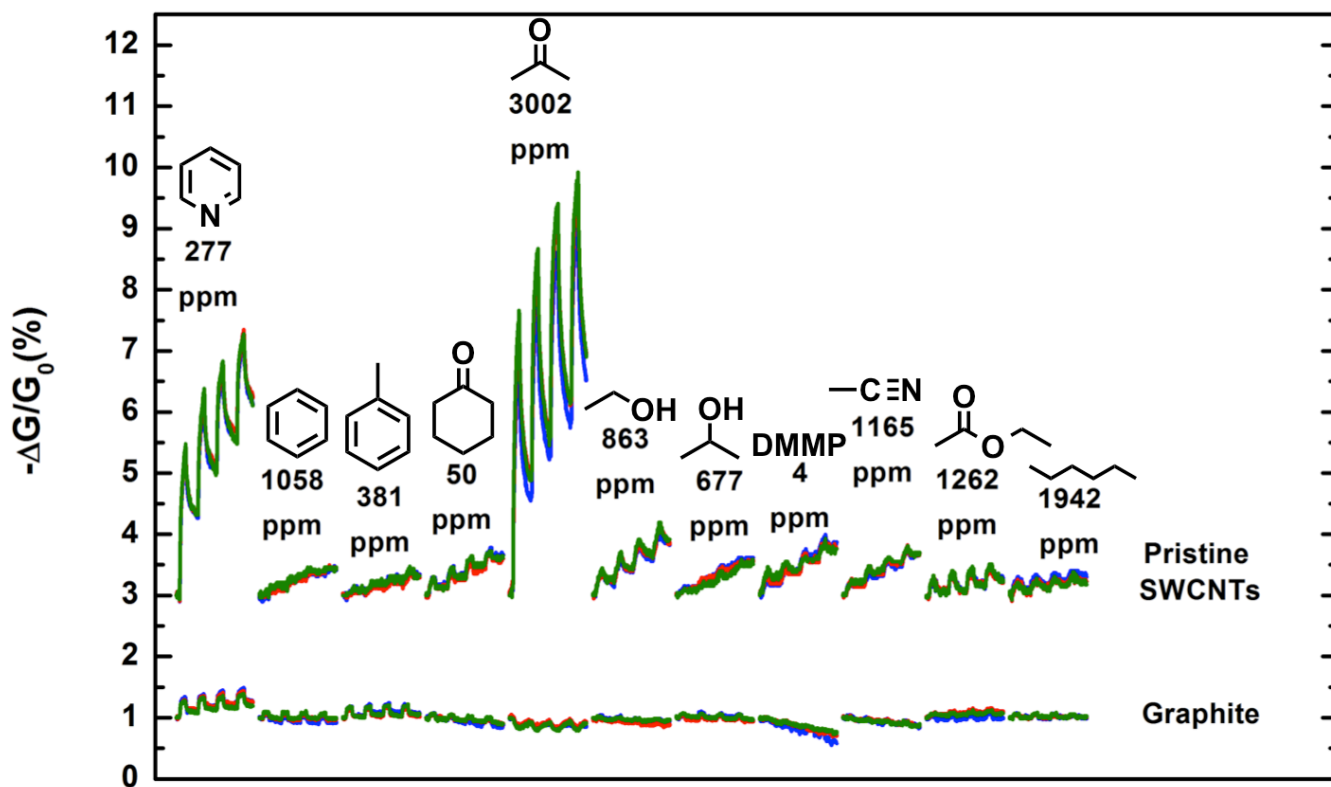


Figure S12. Comparison of sensing responses from graphite and pristine SWCNTs deposited on the surface of weighing paper between gold electrodes. Resistance range of the sensors was between 1-2 k Ω . Normalized change of conductance over time for three devices simultaneously exposed four consecutive times to various analytes for 30 s with a recovery time of 60 s.

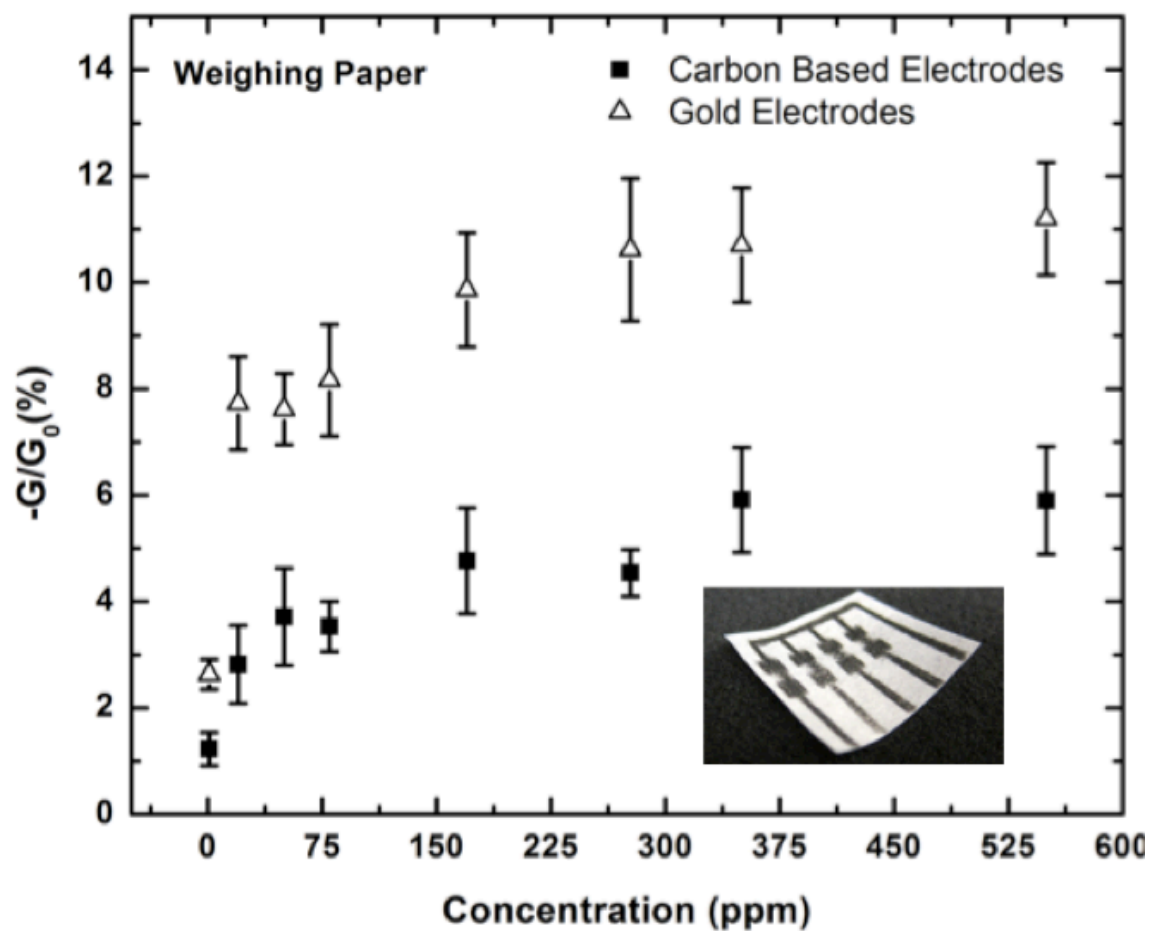
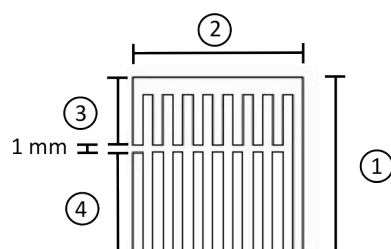


Figure S13. Normalized average conductive response (first exposure exempt) of at least four devices simultaneously exposed five consecutive times to various concentrations of pyridine for 30 s with recovery time of 60s. The devices were fabricated by depositing SWCNT:TEC (2:1 mass ratio) between carbon-based electrodes or gold electrodes by abrasion onto weighing paper. The carbon-based electrodes were fabricated by depositing graphite by abrasion on weighing paper.

Material	Power	Speed	Pulses-per-inch (PPI)
Weighing paper	15	100	1000
PMMA	20	50	500
Glass	10	10	1000

Table S2: Parameters used in laser-etching



	Laser-Etched Weighing Paper		Laser-Etched PMMA		Adhesive Tape		Unpolished Silicon Wafer	
	Distance (cm)	Resistance (k Ω)	Distance (cm)	Resistance (k Ω)	Distance (cm)	Resistance (k Ω)	Distance (cm)	Resistance (k Ω)
1	2.2	7-8.4	2.2	2-2.6	1.7	8-9.9	2.2	4-4.8
2	2.2	5-6.5	2.2	2-2.5	2	8-9.7	2.2	3-3.7
3	0.8	2.8-5.5	0.8	0.8-1.2	0.7	2.6-3.2	0.8	2.1-2.4
4	1.3	4.2-6.5	1.3	1.6-2.3	0.9	2.7-3.2	1.3	2.7-3.8

Table S3. Resistive measurements of carbon-based electrodes used for chemiresistive sensors. Resistance ranges were derived from at least 2 drawn conductive lines. Functionalized SWCNTs with graphite electrodes (drawn within this range or below) had similar sensory performance as functionalized SWCNTs with gold electrodes.

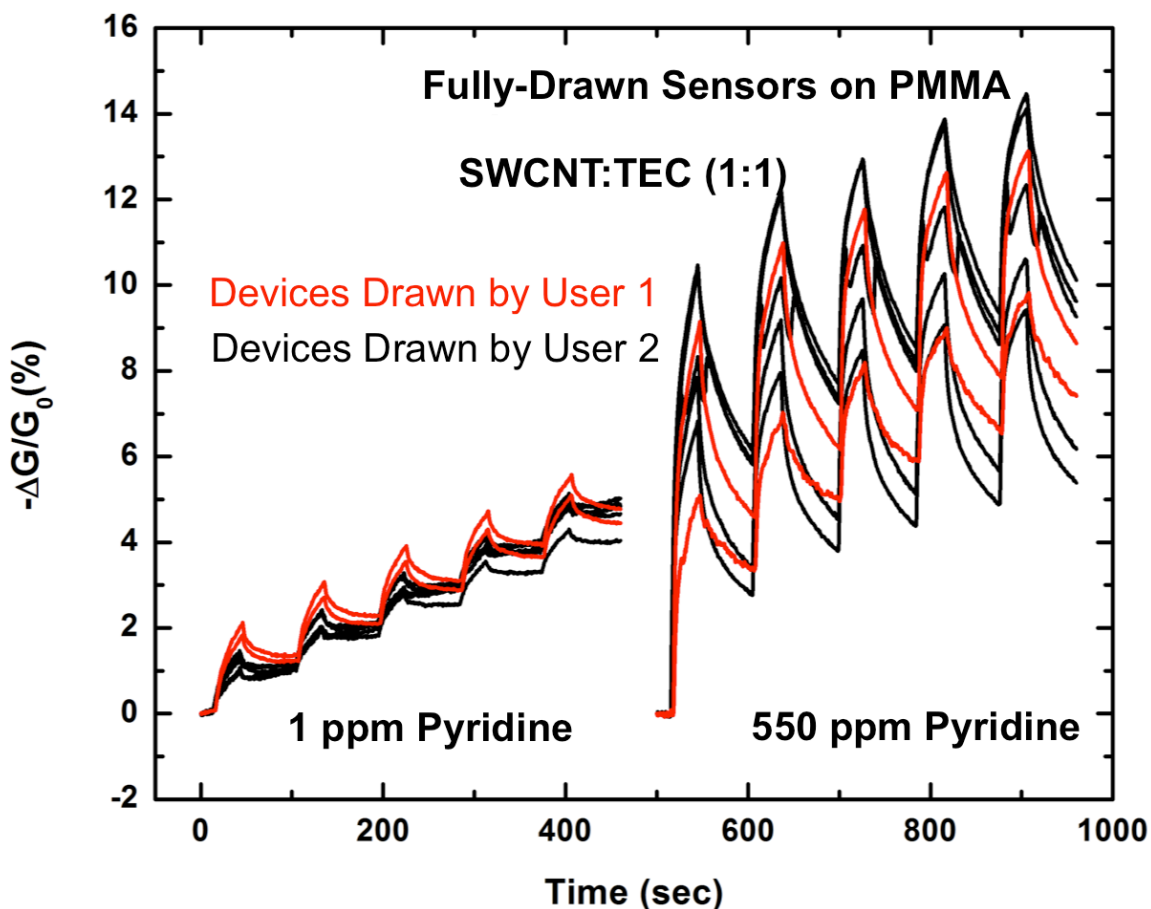


Figure S14. User-to-user reproducibility for fully-drawn carbon-based chemiresistors. Normalized change of conductance over time of 2 devices from user 1 and 5 devices from user 2 simultaneously exposed five consecutive times to 1 and 550 ppm pyridine for 30 s with a recovery time of 60s. The devices were fabricated by depositing SWCNT:TEC (1:1 mass ratio) between carbon-based electrodes. The carbon-based electrodes were fabricated by depositing graphite by abrasion onto laser-etched PMMA.

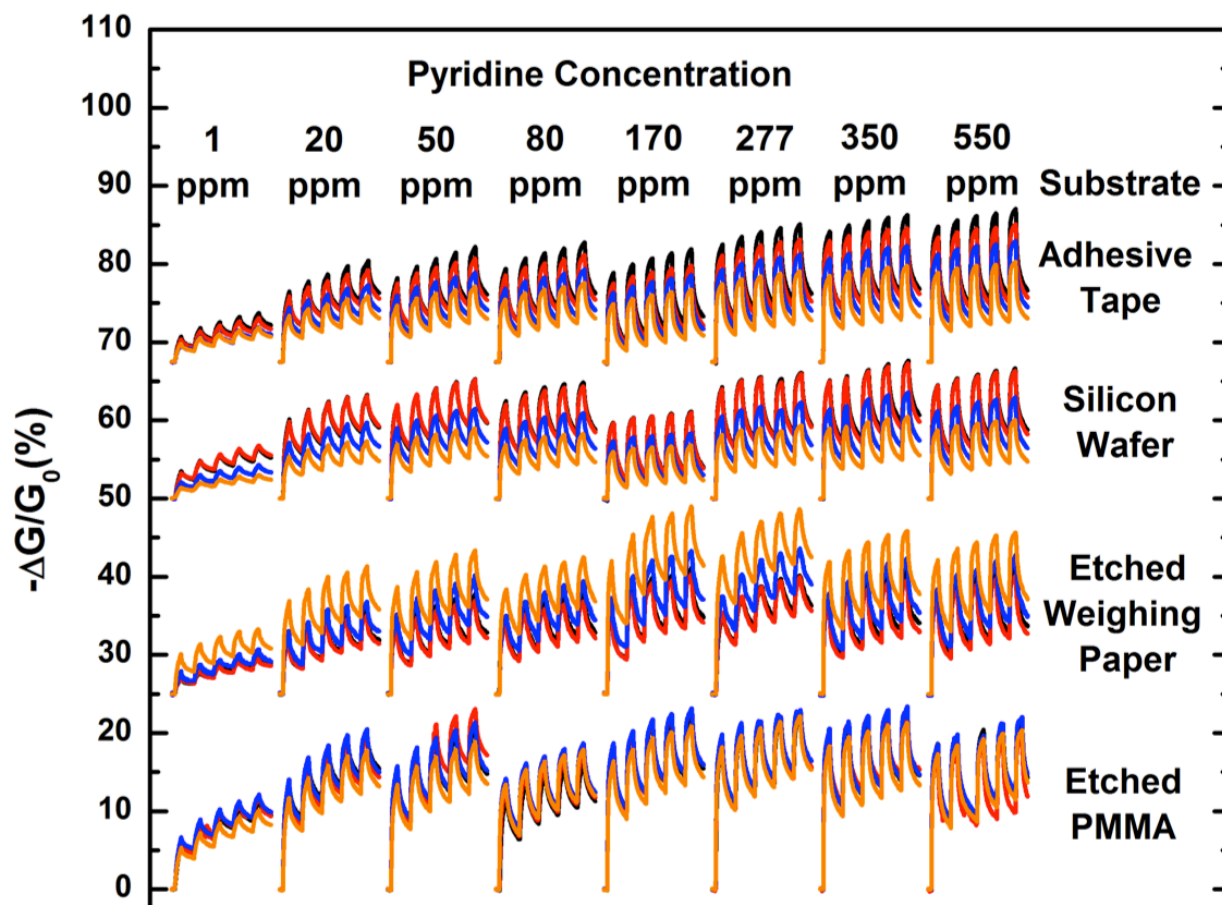


Figure S15. Sensing response traces of four fully drawn devices on various substrates. Normalized change of conductance over time for three devices simultaneously exposed five consecutive times to various concentrations of pyridine for 30 s with recovery time of 60s. The devices were fabricated by depositing SWCNTs-TEC (2:1 wt. ratio) as the sensing material and graphite as the electrode by abrasion on various modified (PMMA and weighing paper) and unmodified (adhesive tape and silicon wafer) substrates.

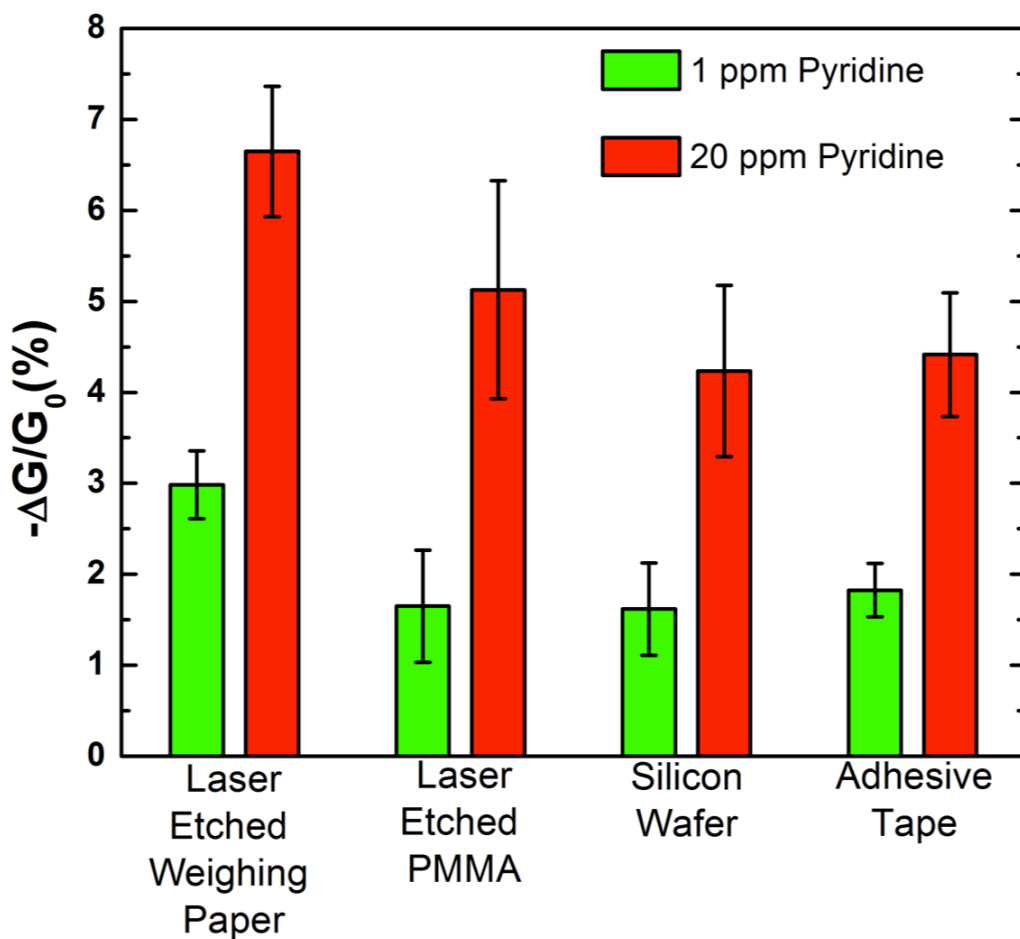


Figure S16. Discrimination of pyridine threshold value limit (1 ppm). Average normalized conductive response (first exposure exempt) of at least four sensors simultaneously exposed to 1 ppm and 20 ppm of pyridine for 30 s with 60 s recovery time. SWCT:TEC (1:2 wt. ratio) pellet was deposited by mechanical abrasion between carbon-based on non-etched substrates (adhesive tape and silicon wafer) and laser etched substrates (weighing paper and PMMA).

Silicon						Adhesive Tape					
Device -ΔG/G ₀ (%)	Exposure (50 ppm Pyridine)					Device -ΔG/G ₀ (%)	Exposure (50 ppm Pyridine)				
	1	2	3	4	5		1	2	3	4	5
1	12.0578244	7.13626659	6.53132438	6.60309686	6.03916469	1	10.7284573	7.55385452	7.19954479	7.00113972	7.00113296
2	12.0213998	6.90612895	6.34005908	6.42240133	5.92836744	2	10.0678072	6.61992556	6.24066438	6.11423486	6.06827194
3	9.06397735	5.40067357	4.95622924	5.05050492	4.68686923	3	8.47276308	5.80278056	5.53577552	5.4289752	5.44678233
4	6.93655398	4.42295678	4.03625483	4.07250598	3.84290386	4	7.22221857	5.02057513	4.79424428	4.69136127	4.73251055
5	11.576235	6.34017367	5.64247918	5.39863107	5.22928493	5	7.51670274	4.51002032	4.28730605	3.98107227	3.8697085
6	12.2462783	6.51781224	5.98782829	5.60442282	5.5705904	6	9.99798978	6.09503192	5.45345129	5.15938846	4.97226741
7	13.8777949	6.48214217	5.71084549	5.40452307	5.23494213	7	8.36486207	5.22502329	4.87883361	4.23476373	4.41188563
8	13.5554758	6.24504274	5.5423308	5.29865366	5.15697525	8	13.9947391	8.11433001	7.75295826	6.73456479	6.70170783
Average Response	11	6.2	5.6	5.5	5.2	Average Response	10	6	5.8	5	5
Standard Deviation	2	0.9	0.8	0.8	0.7	Standard Deviation	2	1	1	1	1
Overall Coefficient of Variance	39%		Overall Coefficient of Variance (first exposure exempt)		15%	Overall Coefficient of Variance	32%		Overall Coefficient of Variance (first exposure exempt)		20%
PMMA						Weighing Paper					
Device -ΔG/G ₀ (%)	Exposure (50 ppm Pyridine)					Device -ΔG/G ₀ (%)	Exposure (50 ppm Pyridine)				
	1	2	3	4	5		1	2	3	4	5
1	8.01757226	5.36252658	4.7921851	5.09374223	4.77251643	1	13.6962788	8.3094539	7.04871158	6.81948135	6.87679062
2	12.3745288	6.666992	5.99290704	5.73706107	5.67801247	2	16.3455903	9.74897433	8.58144012	8.17279515	8.05604242
3	12.0066484	6.44994052	5.7540495	5.45284176	5.38013746	3	16.8236341	9.50342395	8.34760936	7.91951741	7.79109697
4	8.45116782	4.77857169	4.35390648	4.12991831	4.11125337	4	15.4873855	8.51063428	7.47154933	7.22414731	7.02622805
5	8.81863876	6.48919016	6.07320727	5.9900107	5.82361755	5	15.1340237	8.82474102	10.1855653	7.25773135	7.09278503
6	8.41514523	6.10098046	5.82048253	5.61009905	5.4698434	6	15.8329512	9.04084507	7.89353096	7.57227863	7.34281581
7	10.2040879	7.1428583	6.29251494	6.29252305	6.29251494	7	13.5749072	8.00432635	6.92266167	6.6522455	6.65223906
8	13.7404541	8.53574204	7.8417769	7.63359001	7.28660744	8					
Average Response	10	6	6	6	6	Average Response	15	8.8	8	7.4	7.3
Standard Deviation	2	1	1	1	1	Standard Deviation	1	0.6	1	0.6	0.5
Overall Coefficient of Variance	32%		Overall Coefficient of Variance (first exposure exempt)		18%	Overall Coefficient of Variance	34%		Overall Coefficient of Variance (first exposure exempt)		12%

Table S4. Device-to-device variance of fully-drawn sensors on 4 different substrates. Normalized average conductive response to 50 ppm pyridine 5 consecutive times for 30 s with recovery time of 60 s. Devices were fabricated by depositing SWCNT:TEC (2:1 mass ratio) between graphite electrodes onto silicon, adhesive tape, and laser-etch substrates (weighing paper and PMMA).

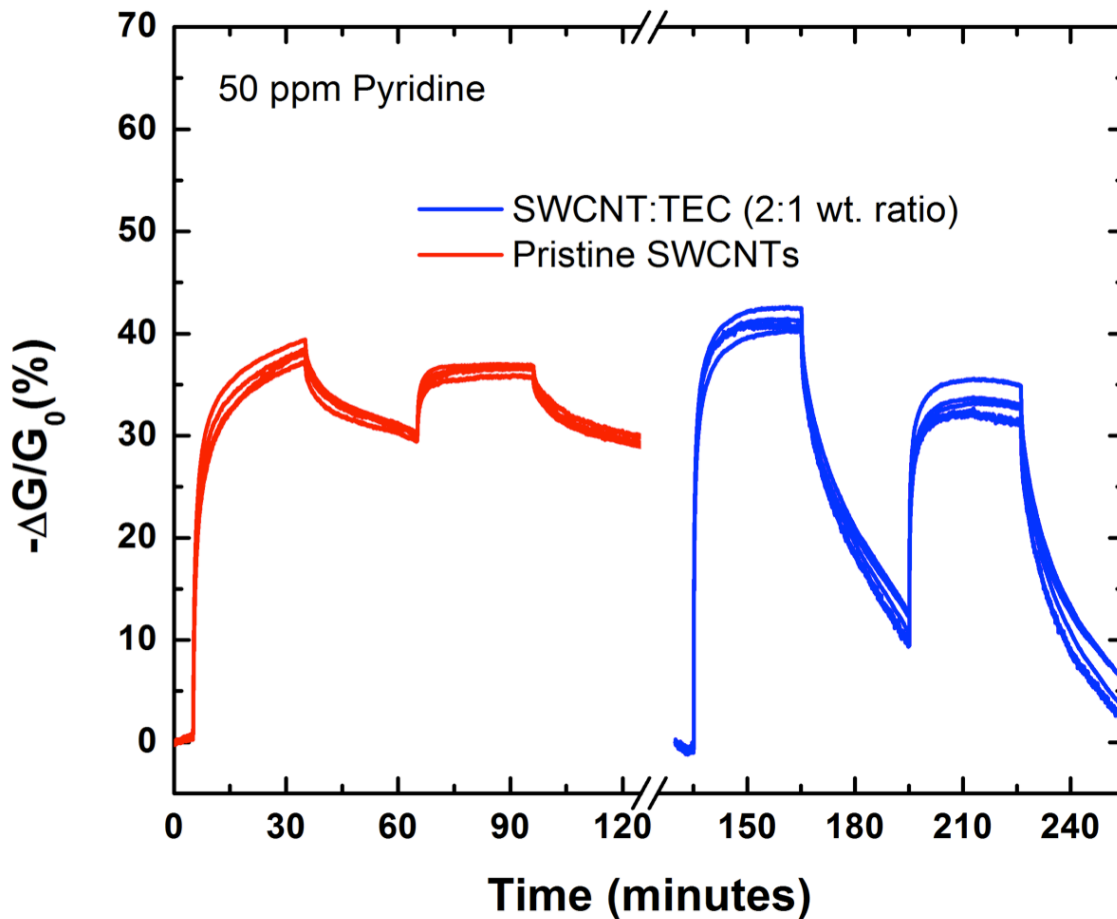


Figure S17. Investigation of sensing material's level of saturation towards pyridine vapor. PENCILs were deposited onto the surface of weighing paper between gold electrodes by abrasion. Resistance range of the sensors was between 100-200 k Ω . Normalized change of conductance over time for three devices simultaneously exposed 2 consecutive times to 50 ppm pyridine for 30 min with recovery time of 30 min.

Principle Component Analysis (PCA) Data

Analyte	Chip #1 (- $\Delta G/G_0$ %)				Chip #2 (- $\Delta G/G_0$ %)			
	1L	2L	3L	1S	1L	2L	3L	1S
20 ppm Aniline	3.4998	4.0516	3.6254	0	3.3014	3.7777	3.0573	0
20 ppm Pyridine	6.2208	4.7428	4.9264	2.0746	5.9505	4.7035	4.3998	1.9809
20 ppm Triethylamine	5.6991	1.574	1.6256	3.0164	5.611	1.8037	1.6026	2.7151
381 ppm Toluene	2.2031	0.6984	1.0727	0.6223	2.035	0.6515	0.6662	0.4348
112 ppm m-Xylene	3.3803	0.7532	0.9402	1.1403	3.1614	0.8528	0.578	1.1362
1050 ppm Benzene	1.1924	0.7027	0.7014	0	1.2877	0.5016	0.7824	0.4932
1942 ppm Hexane	1.5517	0	0	0.7222	1.6472	0	0	0.65
20 ppm DMMP	1.7806	0.9568	0.8761	1.8728	2.1472	0.8766	0.7754	1.9125
3002 ppm Acetone	1.4481	0	0.6461	2.9139	1.6929	0.9648	0.6594	2.8587
1262 ppm Ethyl Acetate	1.0999	0.7478	0.3035	1.7982	1.242	0.6078	0.3362	1.5855

Table S5. Average Sensory Response of Array

	Analyte	Principal Component Scores			
Chip #1 (- $\Delta G/G_0$ %)	20 ppm Aniline	3.02041886	-2.2582316	0.16862097	-0.0523087
	20 ppm Pyridine	5.93957538	0.01273108	0.40486797	0.32616433
	20 ppm Triethylamine	2.10436342	2.49164718	-0.6514034	-0.0291783
	381 ppm Toluene	-1.0189453	-0.5285157	-0.4579539	0.30565414
	112 ppm m-Xylene	-0.295261	0.44041291	-0.8795789	0.12017623
	1050 ppm Benzene	-1.8842341	-1.3814037	-0.3313354	0.07221962
	1942 ppm Hexane	-2.3889098	-0.2245515	-0.5225976	-0.0097312
	20 ppm DMMP	-1.1518008	0.18432001	0.64423895	-0.0218121
	3002 ppm Acetone	-1.9531439	1.21638674	1.14113892	0.43459919
	1262 ppm Ethyl Acetate	-2.0045452	0.03376882	0.78996348	-0.2851886
Chip #2 (- $\Delta G/G_0$ %)	20 ppm Aniline	2.43645335	-2.1016593	0.04042156	-0.2872058
	20 ppm Pyridine	5.46054595	-0.0297108	0.3509106	-0.0294911
	20 ppm Triethylamine	2.14737117	2.14641303	-0.7209601	-0.1904269
	381 ppm Toluene	-1.3811679	-0.6236774	-0.604803	0.04287467
	112 ppm m-Xylene	-0.5688699	0.39697562	-0.8148094	-0.2086747
	1050 ppm Benzene	-1.8619098	-0.9127429	-0.1163166	0.25382786
	1942 ppm Hexane	-2.3348963	-0.2340929	-0.6289596	-0.0116566
	20 ppm DMMP	-1.0221521	0.44393529	0.38518922	-0.0569804
	3002 ppm Acetone	-1.2493162	0.94818345	1.27700276	-0.2042837
	1262 ppm Ethyl Acetate	-1.9935757	-0.0201882	0.52636351	-0.168578

Table S6. Principle Component Scores

Principle Component Coefficient			
0.73209117	0.25912844	-0.6295497	-0.0237101
0.4423137	-0.499677	0.33376159	-0.6657963
0.42100412	-0.4312922	0.2839683	0.74572417
0.30192159	0.70509743	0.64158584	-0.0069694

Table S7. Principle Component Coefficient

Hotelling's T² Statistic
5.11362545
8.20499205
6.03780699
3.05248265
2.23169517
2.25655176
1.50846816
1.16644824
9.0487706
3.94479193
5.99264882
4.7774959
5.98922314
1.4272243
2.68904729
2.67792425
1.74917323
0.70712322
5.52751278
1.89699407

Table S8. Hotelling's T² Statistic

Principal Component Eigenvalues
19.7631869
6.26920716
2.90945992
0.90057793

Table S9. Principal Component Eigenvalues

Percentage of the Total Variance
66.2251219
21.00769525
9.749406226
3.01777662

Table S10. Percentage of the Total Variance