Supplementary Information

Facile Electrodeposition Based Chemosensors Using PANI and C-Hybrid Nanomaterials for the Selective Detection of Ammonia and Nitrogen Dioxide at Room Temperature

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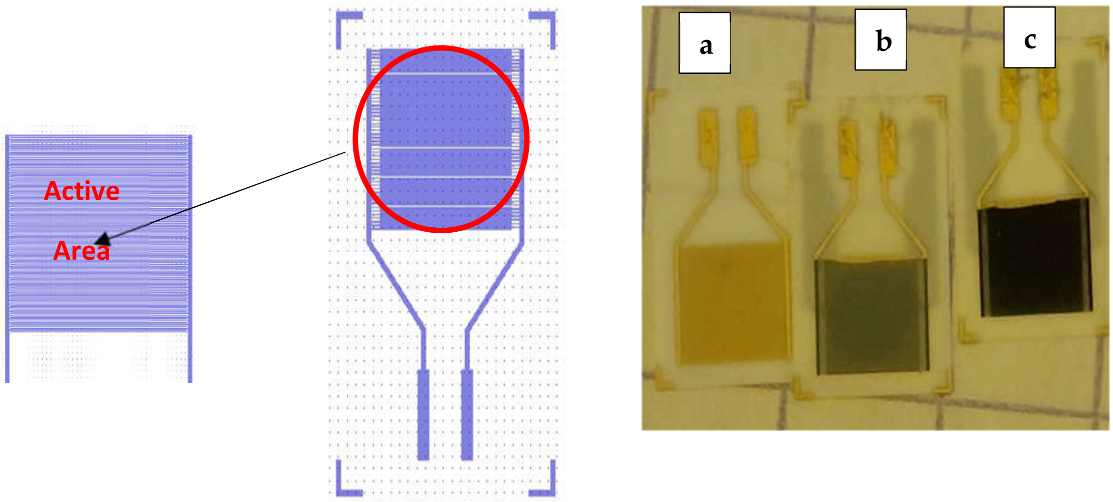


(**A**) (**B**)

Figure S1. (**A**) Interdigitated electrode layout on ceramic substrate (Al_2O_3), (**B**) a. Fabricated sensor; b–c. sensors with electrodeposited films.

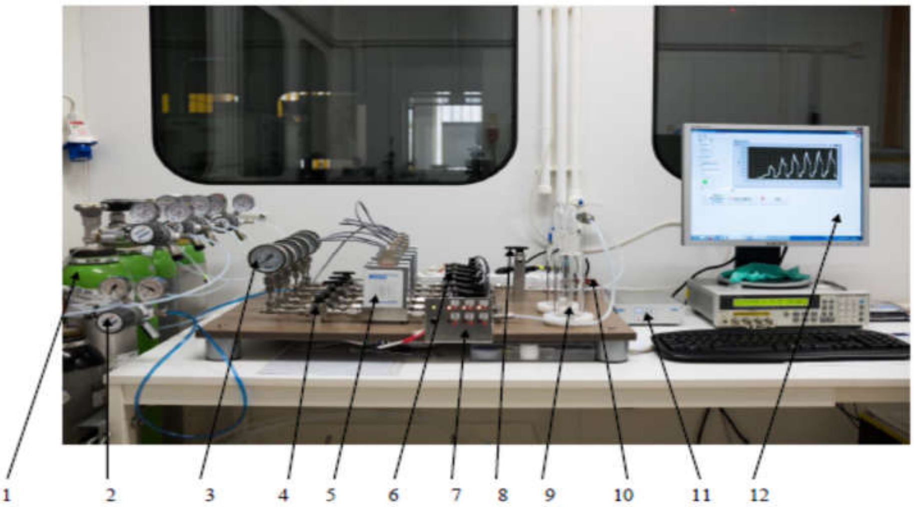


Figure S2. Diagram of testing platform Five gas supply cylinders with the following characteristics: 1. Nitrogen-N (99.999%), as a carrier gas in a 10L/200bar cylinder - Mixture 1000ppm carbon monoxide-CO in nitrogen in a 10L/150bar bottle - Mixture of 100ppm nitrogen dioxide-NO2 in air in a 10L/150bar bottle - 500ppm ammonia-NH3 mixture in nitrogen in a 10L/150bar bottle - 20ppm formaldehyde-CH_2O mixture in nitrogen in a 10L/150bar bottle; 2. Five Pressure Regulators of which: - a chromed brass regulator 200/4bar for the nitrogen cylinder - Four INOX 200/4bar regulators for the other cylinders; 3. Six INOX Manometers, 0-2.5bar for gas pressure monitoring 4. Six INOX ball valves that allow/block the circulation of gases to the test chamber 5. Six MASS FLOW CONTROLLERs that regulate the mass flow. 6. Six electro valves that allow/block the circulation of gases towards the test chamber 7. The control circuit of the solenoid valves 8. A three-way ball valve that allows access of the humidified gas to the test chamber or exhaust of the gas to the outside 9. Bubbler (humidifier) that allows gases to be humidified for sensor testing 10. The test chamber that allows the testing of four sensors to a gas or to a mixture of gases; 11. Controller for controlling flow controllers 12. Interface for data acquisition and definition of test routines.

Table S1. Metrics employed for the PCA. One vector is composed of all elements in the table. Hence metrics are collected for each tested film.

M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12	M13
Formaldehyde mean resistance					Formaldehyde resistance Std					Nitrogen dioxide mean		
40 ppb	80 ppb	120 ppb	160 ppb	200 ppb	40 ppb	80 ppb	120 ppb	160 ppb	200 ppb	8 ppm	16 ppm	32 ppm
M14	M15	M16	M17	M18	M19	M20	M21	M22	M23	M24	M25	M26
resistance		Nitrogen dioxide resistance Std					Carbon monoxide mean resistance					
60 ppm	90 ppm	8 ppm	16 ppm	32 ppm	60 ppm	90 ppm	2 ppm	10 ppm	20 ppm	40 ppm	50 ppm	100 ppm
M27	M28	M29	M30	M31	M32	M33	M34	M35	M36	M37	M38	M39
	Carbon monoxide resistance Std							Ammonia mean resistance				
200 ppm	2 ppm	10 ppm	20 ppm	40 ppm	50 ppm	100 ppm	200 ppm	5 ppm	10 ppm	20 ppm	50 ppm	100 ppm
M40	M41	M42	M43	M44	M45	M46	M47	M48	M49	M50	M51	M52
		Ammonia resistance Std							Mean	Std	Mean	Std

150 ppm	300 ppm	5 ppm	10 ppm	20 ppm	50 ppm	100 ppm	150 ppm	300 ppm	Air	Air	N_2	N_2

Table S2. Initial values of PANI-MWCNT-NH_2 (10 CV cycles and 15 CV cycles) film resistances in air and nitrogen at different humidity values

No.	Cycles no.	RH	R_{air} (kΩ)	R_{N2} (kΩ)	R_{N2} - R_{air} (kΩ)
1.	**10**	10%	1.88	2.78	0.9
	15	10%	2.10	3.60	1.5
2.	**10**	25%	7.70	10.30	2.6
	15	25%	6.00	9.70	3.7
3.	**10**	50%	8.80	12.70	3.9
	15	50%	6.40	10.80	4.4

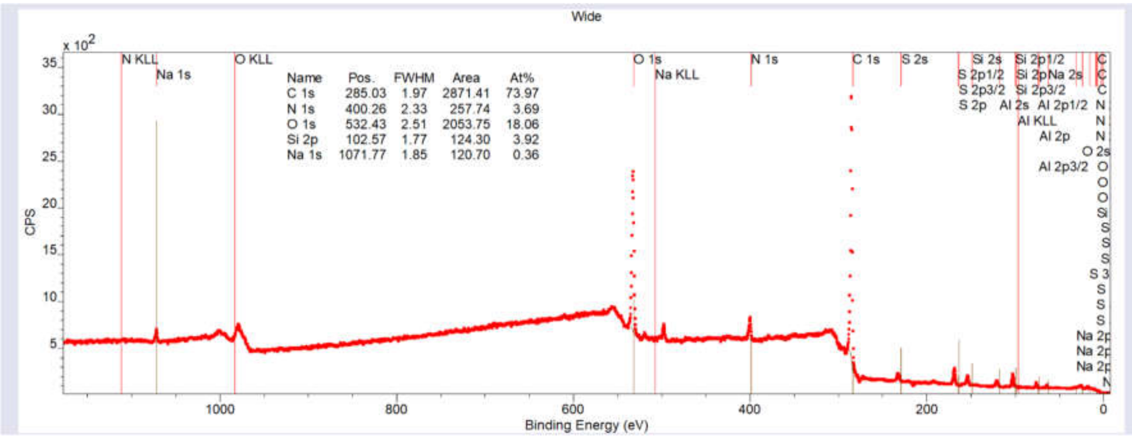


Figure S3. XPS survey spectra of the PANI-MWCNT-NH_2 film.

Tabel S3. The component for C 1s spectra of PANI and PANI-MWCNT-NH_2.

Component	**C-C, C-H**	**C-O, C-N**	**C=O**	**O-C=O**	**Aromatic**
PANI-MWCNT-NH_2	79.17	14.39	4.88	1.38	0.17
PANI	63.53	29.34	3.25	0.63	3.25

Tabel S4. The component for O 1s spectra.

Component	C=O	C-O-C, C-O	C-O-H, H_2O
PANI-MWCNT-NH_2	13.15	78.84	8.02
PANI	42.35	-	57.65

Tabel S5. The component for N 1s spectra.

Component	C-NH-	C-N=	C-N^+
PANI-MWCNT-NH_2	67.84	23.82	8.34
PANI	94.66	4.76	0.57

Table S6. Resistance values for PANI-rGO-ZnO (ANI in 1MHCl) films obtained following the electrodeposition of ZnO at 80 °C.

Aniline ratio %	$Zn(NO_3)_2$ ratio %	GO %	Resistance
2	3	0.8	0.4 kΩ
6.5	1.5	2	65.49 kΩ± 6.47 kΩ
6.5	6	2	> 1 MΩ

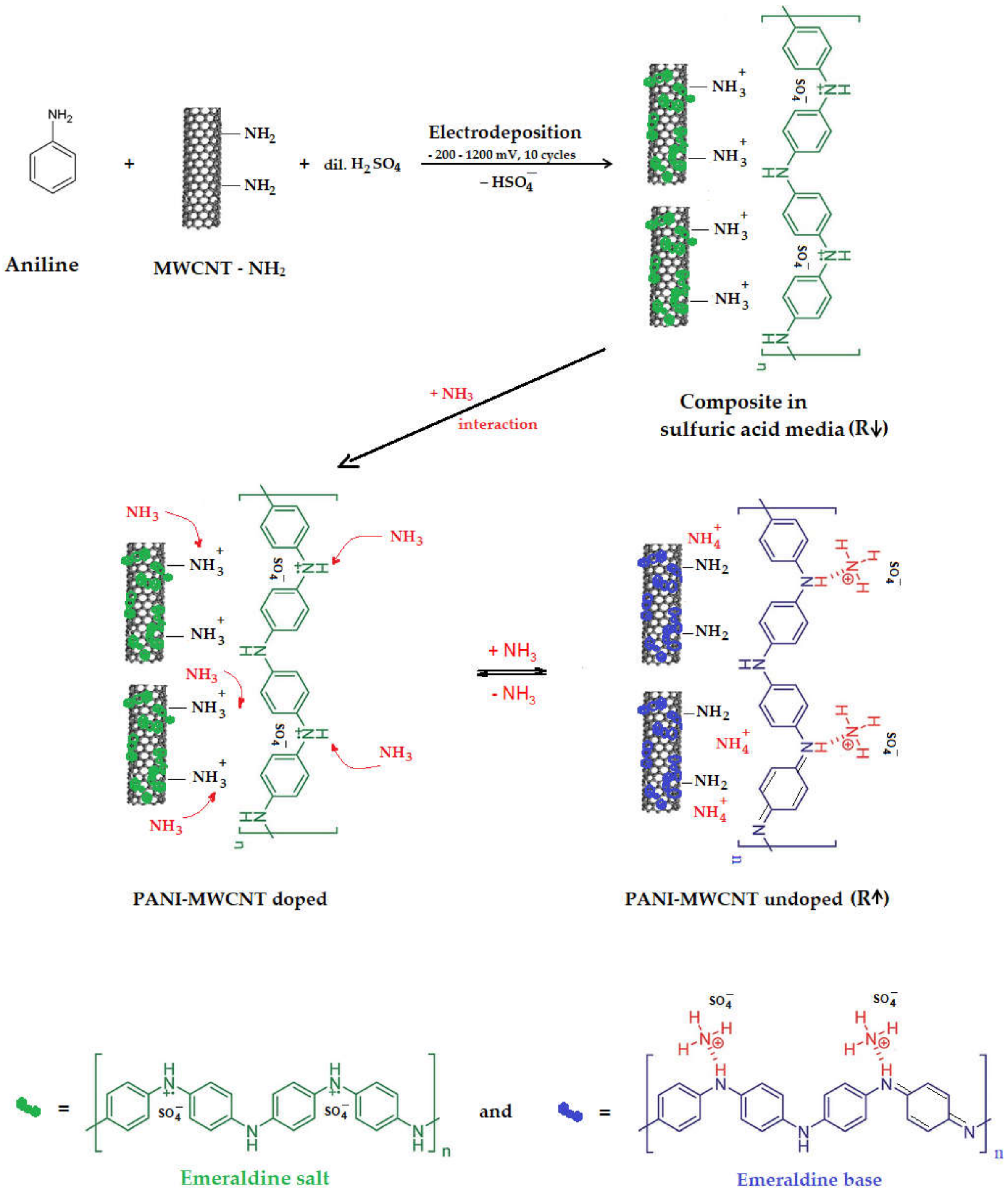
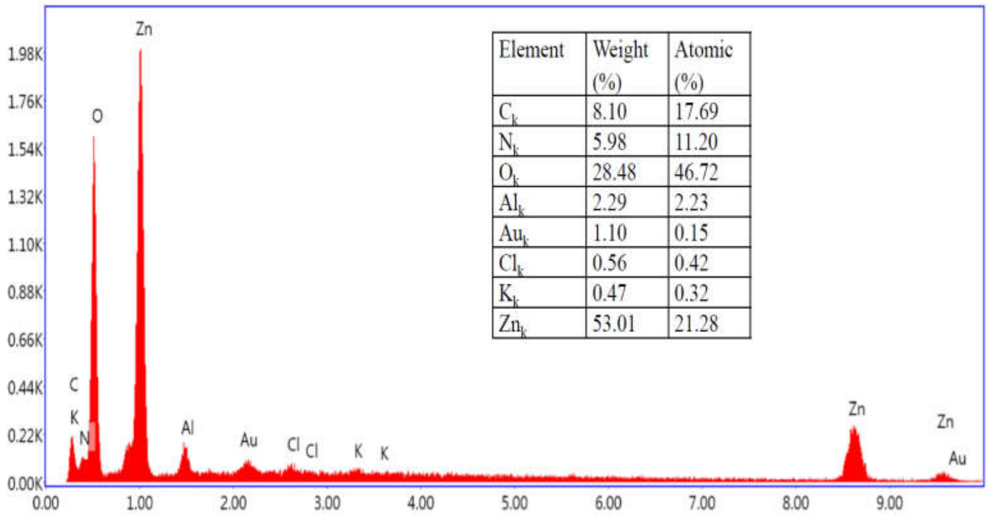
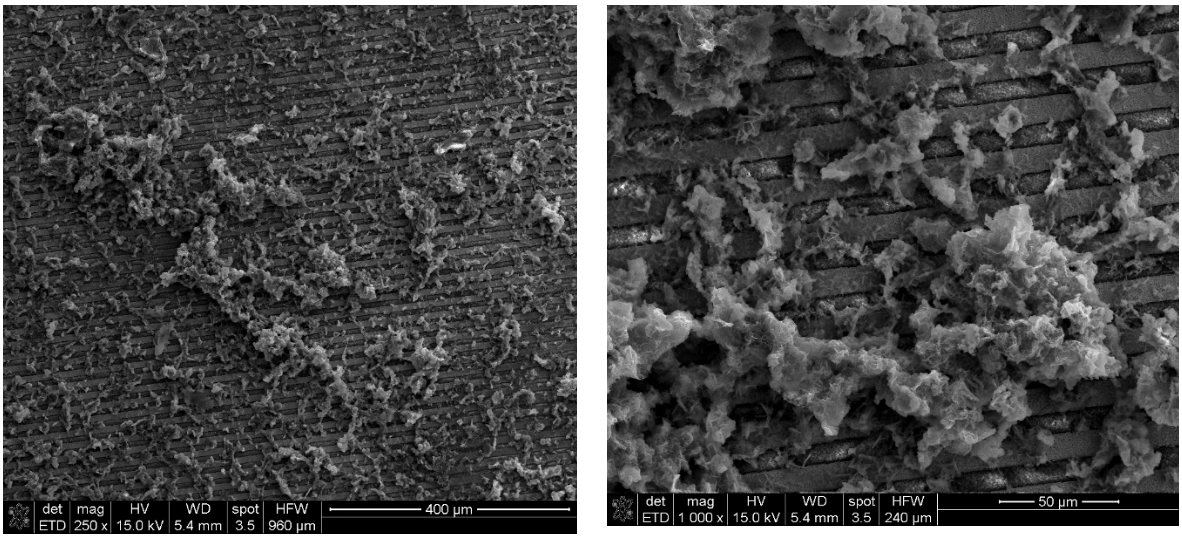


Figure S4. Electrodeposition stage for PANI-MWCNT-NH2 with doped PANI in acidic environments and undoped PANI in basic environments after ammonia exposure.



Element	Weight (%)	Atomic (%)
C_k	8.10	17.69
N_k	5.98	11.20
O_k	28.48	46.72
Al_k	2.29	2.23
Au_k	1.10	0.15
Cl_k	0.56	0.42
K_k	0.47	0.32
Zn_k	53.01	21.28

Figure S5. EDX spectra of PANI-rGO-ZnO.



(**A**) (**B**)

Figure S6. SEM images of the active area of the PANI-rGO-ZnO sensor at different magnifications.

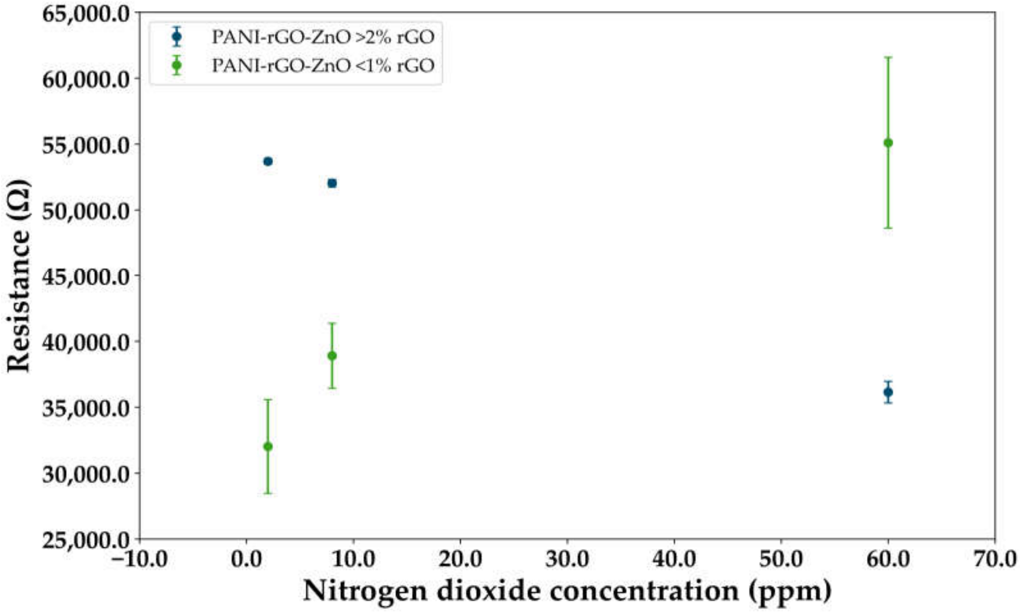


Figure S7. Ressistances changes correlated with %rGO content for PANI-rGO-ZnO.

Table S7. Fabrication protocol for the sensors employed in the selection process.

# Chip	**Sensing Layer**	**Fabrication Details of the Layers**
1	PANI:PSS-SWCNT-COOH	CV: 8 cycles in water solution with ANI 0.1M; polystyrene sulphonate (PSS)- 4% with 0.004%SWCNT-COOH; -0.2 V-0.9V, v=50mV/s
2	PANI-rGO	rGO 1mg/mL reduced with acid ascorbic in CV 10 cycles electrodeposition -600-1600mV, v=50mv/s
3	PANI-rGO	Method from this work for PANI-rGO electrodeposition (presented in the experimental section)
4	PANI-MWCNT-NH_2	CV: 10 cycles 200 mV and 1200 mV with a scanning speed of 50 mV/sec.; 0.5% PSS, 0.007g of MWCNT-NH_2 0.5 M H_2SO_4 and 0.09 M ANI (method detailed in experimental section);
5	PEDOT-rGO	10 mM EDOT with 2mg/mL GO, 30 seconds coulometry at 970mV and 30 seconds GO reduction at -850mV
6	PANI	CV: 15 cycles; 0.10 M ANI in 0.2 M H_2SO4 ; 0.2 V-0.9V
7	Polypirol-reduced graphene-ferocene (PPY-rGO-Fc)	CV 8 cycles 0.2mg/mL GO and 0.1M pyrrole in phosphate buffered saline (PBS) pH 7.4 and 2mM Fc GO reduction with CV 8 cycles between 0.6V—1.5 V, V=25mv/s and 1min Chronoamperometry for Fc electrodeposition at -100mV PPy
8	PPY-GO	CV 8 cycles 0.2mg/mL GO and 0.1M pyrrole in phosphate buffered saline (PBS) pH 7.4 GO reduction with CV 8 cycles between 0.6V—1.5 V, v=25 mv/s 0.1 M PPy (-0.2V-0.8V, 8 cycles v = 100mV/s)
9	PEDOT-MWCNT-NH_2	Solutie in water with: 10 mM EDOT:PEG (21:1,v:v), MWCNT-NH2:PSS (1:66, w:w); 20 seconds Coulometry at 970mV

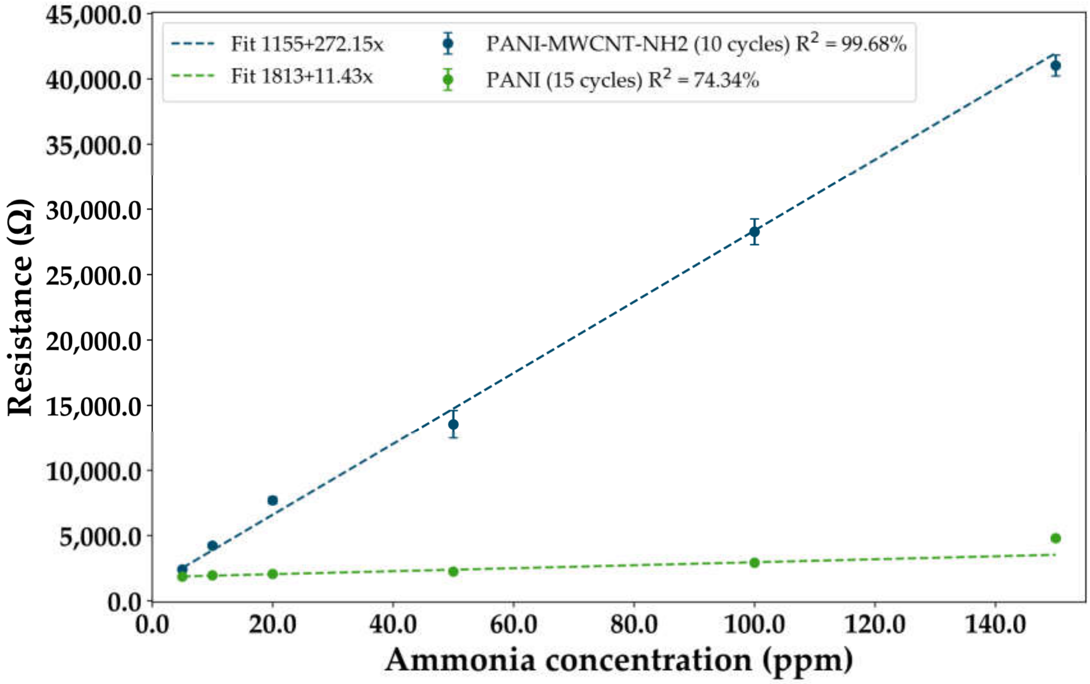


Figure S8. Response and linearity of two sensors, on using only PANI and one adding MWCNT-NH_2 to PANI, on measuring ammonia concentration in a nitrogen atmosphere without added humidity.

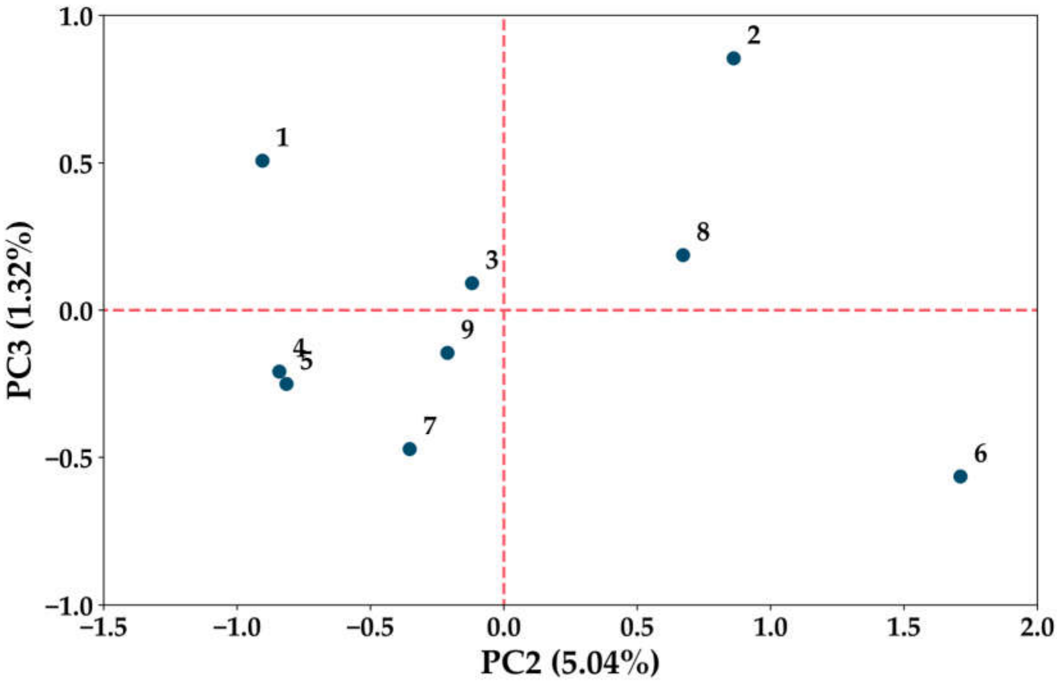


Figure S9. PCA of tested sensors 1-8 to NO_2.