SUPPORTING INFORMATIONS to:

Selective enhancement of graphene ammonia sensing by electrochemical palladium nanoparticle decoration: *ab-initio* insight on the sensing response

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CONTENT:

1. Gas measurement set up

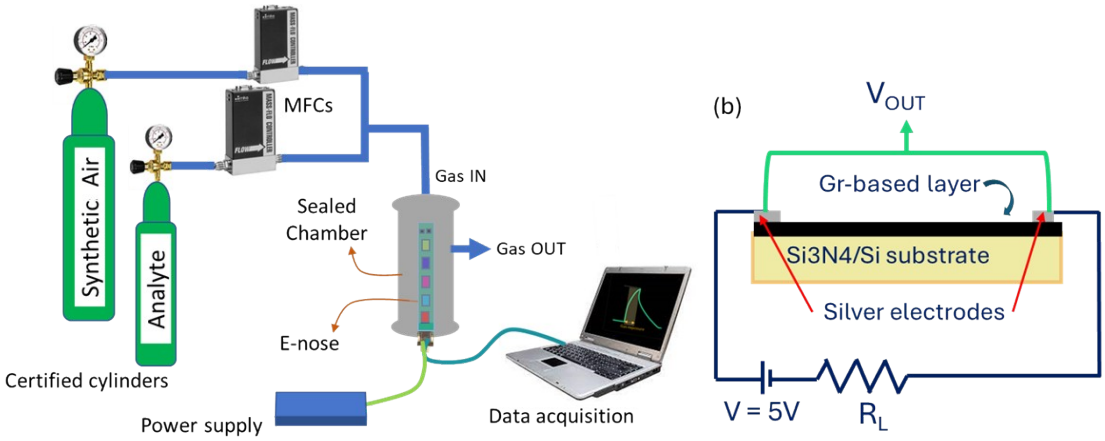

Figure S1: a) Schematic representation of the set up used for the gas exposures. The system comprises a sealed steal homemade chamber, connected to 2 mass flow controllers (MFCs) and a PC for data acquisition, a cylinder filled with synthetic air and a cylinder with the target gas molecules. The sensor array is hosted inside the chamber. The MCF connected to the air cylinder has a maximum flow of 500 sccm, while the max flow of the MFC connected to the analyte cylinders is 200 sccm. b) schematic representation of the readout scheme of each sensor.

2. Raman maps and AFM size distribution

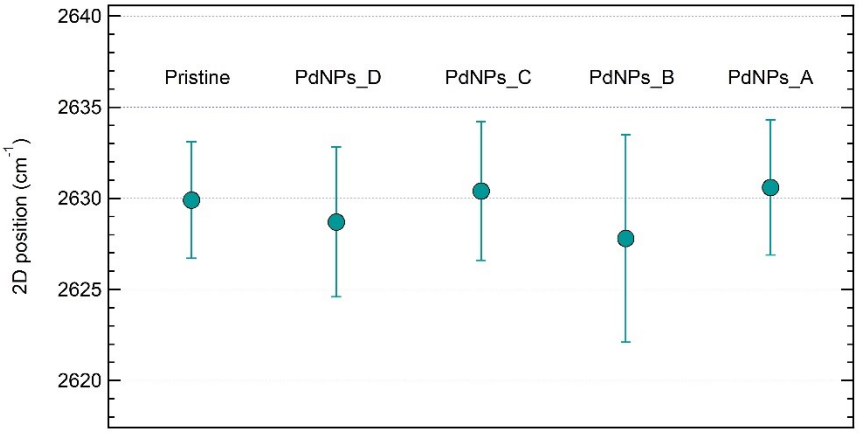

Figure S2. Results obtained from the Raman maps of the 2D-band collected on several areas of the samples. No shift towards higher or lower wavenumber is observed for the decorated samples compared to the pristine position, indicating that the functionalization does not alter the doping nature of the graphene layer.

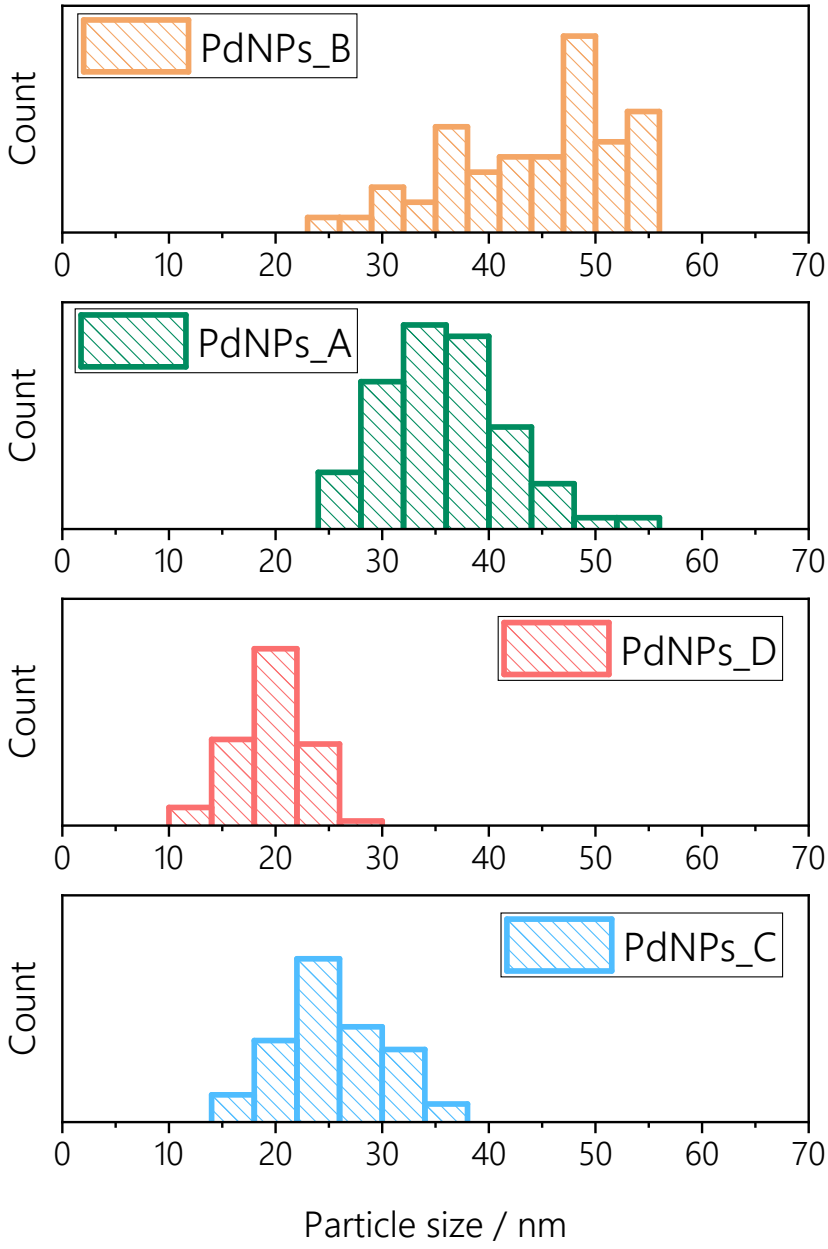

Figure S3: size distribution of the Pd NPs obtained from several AFM images.

3. Benchmarking with literature and Freundlich fitting parameters

Table S1: pow and A parameters obtained from the Freundlich isotherm interpolation of each sensor calibration curve for NH_3 exposures, reported in **Figure 3** of the main text.

Sample name	pow	A
Pristine	0.53 ± 0.09	0.0020 ± 0.0006
PdNPs_D	0.59 ± 0.05	0.0235 ± 0.0002
PdNPs_C	0.59 ± 0.08	0.0210 ± 0.0008
PdNPs_B	0.83 ± 0.07	0.0072 ± 0.0003
PdNPs_A	0.92 ± 0.09	0.0048 ± 0.0007

Table S2: Benchmarking for dynamical tested range, sensitivity S range ($S=(|\Delta R/R_0| \times 100)/[gas]$), detection limit (dl) and response and recovery times of the prepared samples, against the values for other graphene-based chemiresistors reported in the literature.[Refs 14,64-80 in the main text] Of note: only articles reporting gas concentration and sensor response/sensitivity have been taken into account for this benchmarking

Sensor type	Gas: dynamic tested range (ppm)	Sensitivity range (%ppm^{-1})	Detection limit (ppb)	Response time	Recovery time	Reference
PdNPs_A	0.5 – 24.3	0.71 – 0.34	42	100sec @0.92ppm	13min @0.92ppm	Present work
PdNPs_B	0.5 – 24.3	0.87 – 0.39	32	100sec @0.92ppm	15min @0.92ppm	Present work
PdNPs_C	0.5 – 24.3	1.52 – 0.46	13	100sec @0.92ppm	25min @0.92ppm	Present work
PdNPs_D	0.5 – 24.3	2.62 – 0.52	6	100sec @0.92ppm	24min @0.92ppm	Present work
Gr_CoPt	2.2 – 36.0	0.8 – 0.24	0.1	-	15 min @36ppm	77
Gr_CuPR	0.2 – 14.0	0.62 – 0.12	5	30 sec @13.6ppm	700 sec @13.6ppm	80
Gr-NiPc	0.04 - 4.7	8.6 – 0.5	3	132 sec @2.7ppm	11 min @2.7ppm	79
NiPc-Gr	5.0 – 10.0	0.45 – 0.15	-	-	-	78
Gr_NiPc	0.5 – 13.6	0.64 – 0.11	50	-	2.5 min	14

					@3.7ppm	
Gr-TCN	0.85 – 22.5	6.3 – 1.5	4.2	50 sec @11ppm	8 min @11ppm	76
Gr_NBD	0.05 – 8.4	10.78 – 0.45	-	-	-	75
Bare Gr	150 – 1000	0.03– 0.0185	1600	-	-	74
B-doped Gr	16 – 256	0.12 – 0.09	-	0.85 sec @32 ppm	-	73
CVD graphene	100 – 800	0.05-0.01	-	7 min @100ppm	15 min @100ppm	72
Laser written Gr	75 – 400	0.04 – 0.075	-	-	-	71
B-doped Gr	1 – 20	0.04 –0.042	59.9	-	-	70
TiO2@PPy–GN	10 – 200	2.4 –1.3	1000	36 sec @50ppm	16min @50ppm	69
Graphene/mica	20 – 500	0.05 – 0.04	-	-	-	68
graphene–PEDOT:PSS	25 – 1000	0.2 – 0.019	10000	3 min @25 ppm	6 min @25ppm	67
graphene/PANI	1 – 6400	0.05 – 0.20	1000	50 sec @20ppm	23 sec @ 20ppm	66
CVD graphene	0.5 – 1000	0.03 – 0.91	500	-	140 min @10ppm	65
Gr_AuNPs	15 – 58	0.18 – 0.14	-	-	54 min @58ppm	64

4. Theoretical calculation

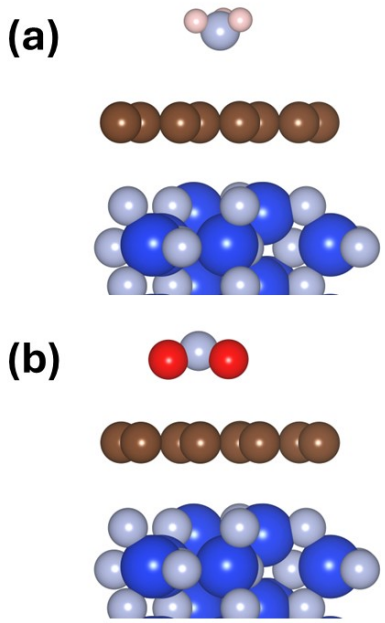

Figure S4: Side view of the adsorption of (a) ammonia and (b) nitrogen dioxide on graphene on Si_3N_4 surface.