Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Unique Modulation Effects of Performance of Graphene-Based Ammonia Sensors via Ultrathin Bimetallic Au/Pt layers & Gate Voltages

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Figure S1. Optical photograph of pristine graphene (a), SEM pictures of channel area of Au/Gr (b), Pt/Gr (c) and Pt/Au/Gr devices (d), XPS full survey-scan spectra of pristine graphene (e), experimental and fitted XPS of Au/Gr surface (f), Pt/Gr surface (g), and Pt/Au/Gr surface (h).

Figure S2. (a) Micro-Raman spectra corresponding to A, B and C positions in Fig.S1(a), (b) micro-Raman spectra of Gr, Au/Gr, Pt/Gr and Pt/Au/Gr.

Figure S3. RT dynamic response curves of (a) Au/Gr, (b) Pt/Gr, and (c) Pt/Au/Gr devices, under the back gate voltage of +60 V upon 3 min exposure to NH_3 with various concentrations.

Figure S4. The polynomial fittings of response versus time plots at baseline for (a) Au/Gr, (b) Pt/Gr, and (c) Pt/Au/Gr devices.

Section S4: Calculations of LOD of Au/Gr, Pt/Gr and Pt/Au/Gr devices.

The LOD of device can be estimated through following formula. [1,2]

$$LOD = 3 \times \frac{RMS}{|Slope|}$$

Here, RMS is the noise level calculated from the polynomial fitting of the $\Delta I/I_0$ versus time plots at baseline before exposure to test gas, and 'Slope' is the slope of calibration curve. The RMS can be estimated through following formula. [1,2]

$$RMS = \sqrt{\frac{\Sigma(a_i - a)^2}{N-1}}$$

Taking N=35 data points at the baseline and regular residual of polynomial fittings (a_i-a).

Figure S5. RT response curves upon 3 min exposure to 5 ppm NO_2 gas under different V_{GS} for (a) Au/Gr, (b) Pt/Gr, and (c) Pt/Au/Gr devices.

Figure S6. RT response curves upon 3 min exposure to 200 ppm NH_3 gas at V_{GS} of +60V tested under different values of RH for (a) Au/Gr, (b) Pt/Gr, and (c) Pt/Au/Gr devices.

Figure S7. RT response curves at different days of devices upon 3 min exposure to 200 ppm NH_3 gas with V_{GS} = +60V and RH=20% for (a) Au/Gr, (b) Pt/Gr, and (c) Pt/Au/Gr devices.

Figure S8. The TDOS (a)~(e) and PDOS (f)~(j) of NH_3-Au/Gr systems under different values of electric field intensity.

Figure S9. The TDOS (a)~(e) and PDOS (f)~(j) of NH_3-Pt/Gr systems under different values of electric field intensity.

Figure S10. The TDOS (a)~(e) and PDOS (f)~(j) of NH_3-Pt/Au/Gr systems under different values of electric field intensity.

Table S1. RT response to 200 ppm NH_3 gas for Au/Gr, Pt/Gr and Pt/Au/Gr devices under different back gate voltages.

V_G	-20 V	0 V	+20 V	+40 V	+60 V
Au/Gr	-9.29%	-10.51%	-12.52%	-15.12%	-16.08%
Pt/Gr	-16.51%	-17.53%	-17.47%	-17.50%	-17.47%
Pt/Au/Gr	-8.23%	-11.03%	-12.47%	-14.68%	-16.18%

Table S2. Response time to 200 ppm NH_3 gas for Au/Gr, Pt/Gr and Pt/Au/Gr devices under different back gate voltages.

V_G	-20 V	0 V	+20 V	+40 V	+60 V
Au/Gr	126 s	120 s	126 s	114 s	114 s
Pt/Gr	108 s	126 s	108 s	108 s	102 s
Pt/Au/Gr	108 s	84 s	66 s	54 s	54 s

Table S3. Recovery time to 200 ppm NH_3 gas for Au/Gr, Pt/Gr and Pt/Au/Gr devices under different back gate voltages.

V_G	-20 V	0 V	+20 V	+40 V	+60 V

Au/Gr	>20 min	28 min	24 min	20 min	12.7 min
Pt/Gr	>20 min	26 min	9.5 min	6.2 min	4.4 min
Pt/Au/Gr	>20 min	20 min	16 min	6.7 min	4.6 min

Table S4. RT responses of different devices at the back gate voltage of +60V upon 3 min exposure to NH_3 with various concentrations.

V_G	12 ppm	25 ppm	50 ppm	100 ppm	200 ppm
Au/Gr	-4.8%	-6.5%	-9.1%	-10.7%	-16.08%
Pt/Gr	-5.64%	-8.91%	-6.12%	-13.53%	-17.47%
Pt/Au/Gr	-6.43%	-7.56%	-9.7%	-12.25%	-16.18%

Table S5. TDOS near near Fermi level of different systems at different electric field strengths.

F(V/Å)	-2	0	2	4	6
NH_3-Au/Gr	26.38	18.95	17.15	10.48	5.97
NH_3-Pt/Gr	22.75	19.18	19.03	20.03	21.56
NH_3-Pt/Au/Gr	27.21	26.84	24.90	13.92	4.834

Table S6. E_{ads} of different systems at different electric field strengths.

F(V/Å)	0	2	4	6
NH_3-Au/Gr	-1.165 eV	-1.078 eV	-0.894 eV	-0.621 eV
NH_3-Pt/Gr	-1.766 eV	-1.231 eV	-0.843 eV	-0.301 eV
NH_3-Pt/Au/Gr	-1.888 eV	-1.564 eV	-1.146 eV	-0.788 eV

Table S7. Comparison of sensing performances to NH_3 gas for Pt/Au/Gr device in this work with those graphene-based gas sensors reported in the literature.

Sensing materials	**Concentration of NH_3**	**Detecting temperature**	**Response time**	**|Response|**	**Recovery time**	**References**
CVD graphene on aluminum oxide substrate	1300 ppm	RT	156 s	1.5%	2.2 min	[3]
Ag-NPs/ Graphene	500 ppm	RT	min	9.5%	—	[4]
Ti-decorated CVD graphene	400 ppm	RT	150 s	17.9%	3 min	[5]
Co(tpfpp)ClO_4 treated graphene	160 ppm	RT	60 s	8.34%	—	[6]
Ester functionalizated graphene oxide	100 ppm	RT	55 s	12%	1.3 min	[7]
3D RGO/PANI hybrid	50 ppm	RT	370 s	10.8%	11.3 min	[8]
α-Fe_2O_3/graphen-e nanohybrid	50 ppm	250℃	70 s	26%	20.3 min	[9]
FMNS-functionali-zed graphene	1000 ppm	RT	15 min	18.5%	16 min	[10]
Au-decorated CVD graphene	200 ppm	RT	114 s	16.08%	12.7 min	This work
Pt-decorated CVD graphene	200 ppm	RT	102 s	17.47%	4.4 min	This work
Pt/Au-decorated CVD graphene	200 ppm	RT	54 s	16.18%	4.6 min	This work

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