Electronic Supplementary Information

Ultra-sensitive IDE-Based Ammonia Sensor Fabricated using Green synthesized Graphene nanoplatelet and TiO_2 based composite

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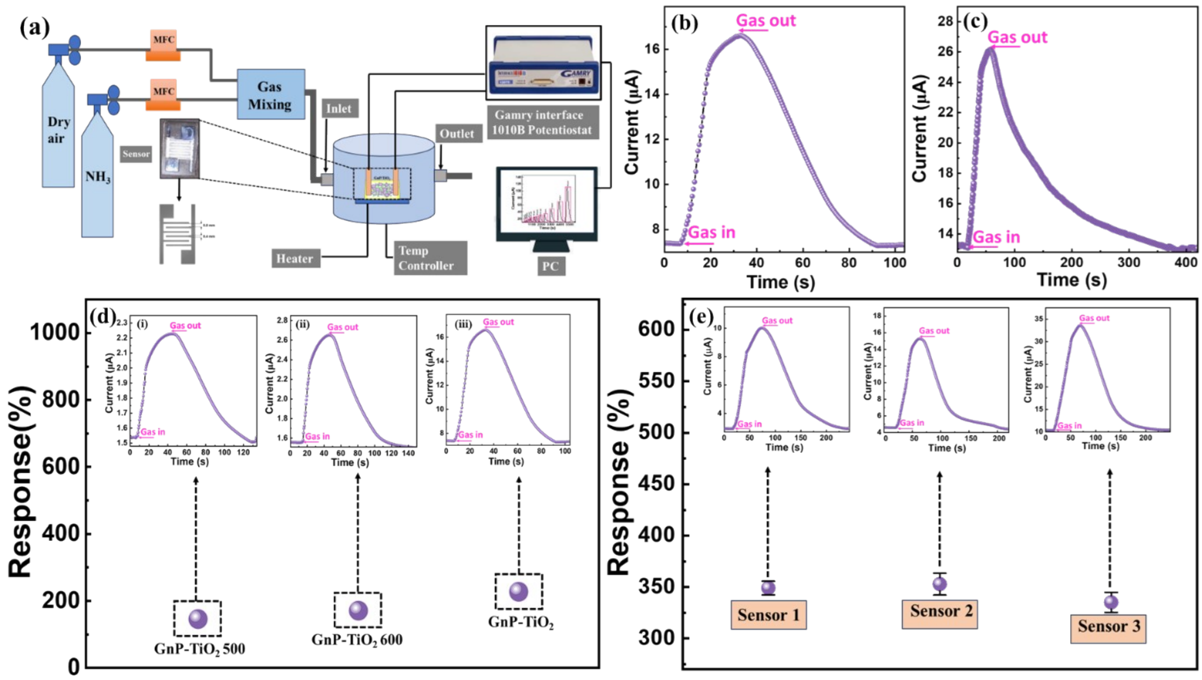

Fig. S1 (a) Schematic diagram of the gas sensing setup for NH_3 sensing. Current vs time plot for NH_3 sensing (b) 5 ml GnP-TiO_2 (c) 10 ml GnP-TiO_2 nanocomposite. (d) Sensing response for three different calcinated GnP-TiO_2 sensors. (e) Reproducibility of the GnP-TiO_2 sensors.

The schematic of gas sensing setup used for the dynamic gas mixing measurements is shown in Figure S1(a).The concentration of the target gas varies using dynamic gas mixing method based on the dilution equation:

$C_1V_1 = C_2V_2$

Where, C_1 and C_2 are concentrations of the Initial NH_3 (inside calibrated gas cylinder) and targeted NH_3 whereas V_1 and V_2 are flow rates (gas volume) of the targeted gas and mixed gas (targeted + base gas) flowing in the chamber. During the measurements a total constant flow rate of 100 sccm was maintained. By adjusting the flow rate of different MFCs, different NH_3 gas concentrations were obtained. For example, a C_2= 50 ppm ammonia concentration will be obtained using C_1= 1000 ppm, C_2=? , V_1=5 sccm, and V_2= 100 sccm.

Fig. S1 (b and c) shows that current as a function of time plots for 5 ml and 10 ml GnP-TiO_2 nanocomposite for 800 ppb NH_3 concentration at room temperature. Both sensors exhibit a reversible sensing behavior upon exposure to NH_3 of concentration of 800 ppb. The calculated sensor response is ~ 227% for 5 ml and ~ 200 % for 10 ml GnP-TiO_2 composite. In addition, the recovery time is noticeably longer for the 10 mL GnP-TiO_2 composite, indicating that excess GnP adversely affects both the sensing response and recovery behavior. Therefore, a sensor made with 5 ml GnP-TiO_2 composite is selected for the study.

The GnP-TiO_2 composite (5 ml GnP) was synthesized using hydrothermal method, followed by calcination at three different temperature at 500, 600 and 700 °C to optimize performance. Gas sensing experiments for 800 ppb NH_3 were independently performed using sensors fabricated by samples that annealed at different calcination-temperature, as shown in Fig. S1(d).

Figure S1(d) shows a comparison of sensing responses of GnP–TiO_2 sensors calcined at different temperatures. A clear increase in sensing response is observed with increasing calcination temperature, with values of 145% inset of Fig. d(i), 176% inset of Fig. d(ii), and 227% inset of Fig. d(iii)for the 500, 600, and 700°C calcined sensors, respectively, at 800 ppb ammonia at room temperature, confirming the superior performance of the 700°C GnP-TiO_2 composite. Therefore, GnP-TiO_2 composite made with 5 ml GnP, and annealed at 700 °C is used for the study. All other characterizations are performed on this sample.

Reproducibility of the GnP-TiO_2 sensors was evaluated by fabricating three GnP–TiO_2 sensors and testing them toward 5 ppm NH_3 concentration at room temperature. The average response obtained from the three observations for each sensor was calculated and plotted in Fig. S1(e). The three sensors exhibited response values of 349 ± 6.55%, 353 ± 10.59% and 335 ± 9.74 % toward 5 ppm NH_3. The calculated average response was ≈345%, with small variation. The F-value of 2.07 with a P-value is 0.206 which is greater than 0.05, indicating that there is not statistically significant variation in response value (Table S1). This result confirms that the proposed model adequately represents the experimental data, demonstrating good reproducibility and reliability of the sensor response. Therefore, the 700 °C–calcinated and 5 ml GnP-TiO_2 sample was selected as the optimized material and used for all detailed sensing studies discussed in the manuscript. The optimized

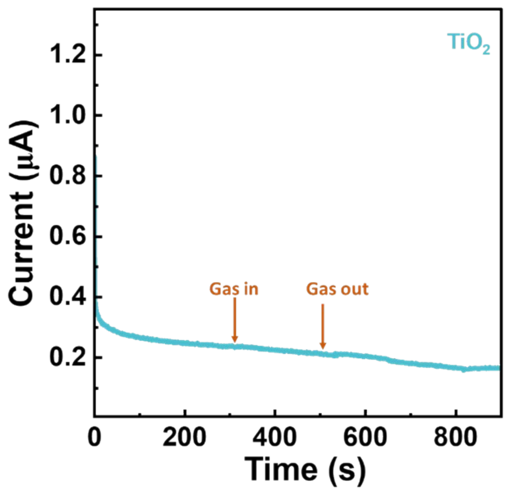

Fig. S2 Current vs time plot for TiO_2 based sensor for NH_3 gas at room temperature.

sample is denoted as "GnP–TiO_2" throughout the paper.

Fig. S2 represents the current vs time plot of TiO_2 nanostructures. It is clearly observed that no significant variation in current upon NH_3 exposure, at room temperature, for 7 V applied voltages. This observation suggests that pure TiO_2 nanostructures do not give any sensing behaviour toward NH_3 at room temperature.

Fig. S3 demonstrates the reproducible behavior of graphene nanoplatelets, where the sensor exhibits a consistent response toward 1 ppm NH_3 over seven consecutive exposure cycles.

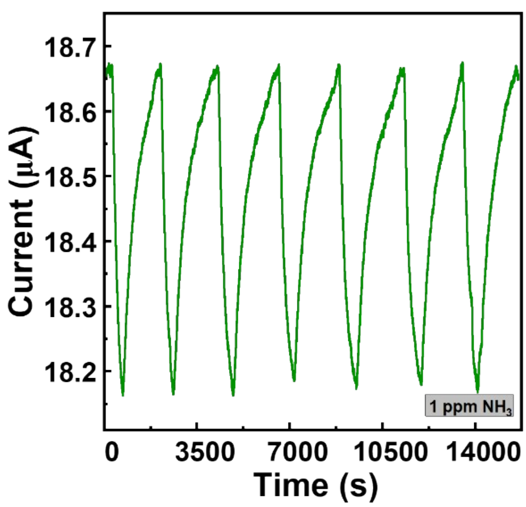

Fig. S3 Response curve of GnP sensor for 1 ppm NH_3 gas concentration.

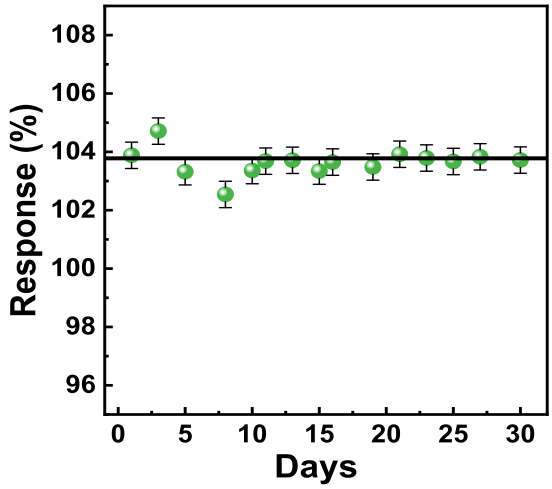

Fig. S4 Stability test for GnP sensor.

The stability of the GnP based sensor was tested for 5 ppm NH_3 over 30 days, exhibiting an average response of 103 ± 0.45 %, indicating good stability over time, as shown in fig. S4.

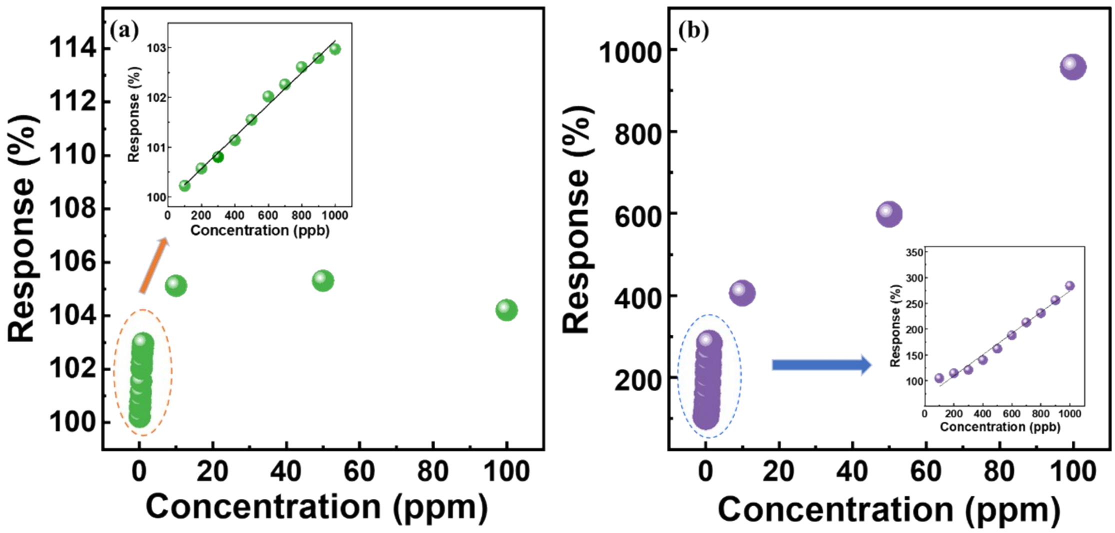

Fig. S5 Response vs gas concentration curve for (a) GnP and (b) GnP-TiO_2 composite material.

Figure S5 represents the response curves from GnP and GnP-TiO_2 based sensor for different ammonia concentrations. The response clearly linear, for both the sensors, in the low concentration range of 100 ppb to 1 ppm {inset of Fig. S5(a & b)}. This linear region was employed to calculate theoretical limit of detection (LOD) using below equation,

$$LOD\ (ppm) = 3\sigma/b \qquad (1)$$

where σ represents the standard deviation of the sensor response and b is the slope of the calibration curve. The calculated LOD ~67 and ~ 91 ppb for GnP and GnP-TiO_2 composite, respectively. The sensitivity of the sensor, represented by the slope (s), was calculated and found to be 0.003 % and 0.206 % per ppb, respectively. The higher sensitivity of GnP-TiO_2 based sensor enable the detection of NH_3 below 100 ppb concentrations.

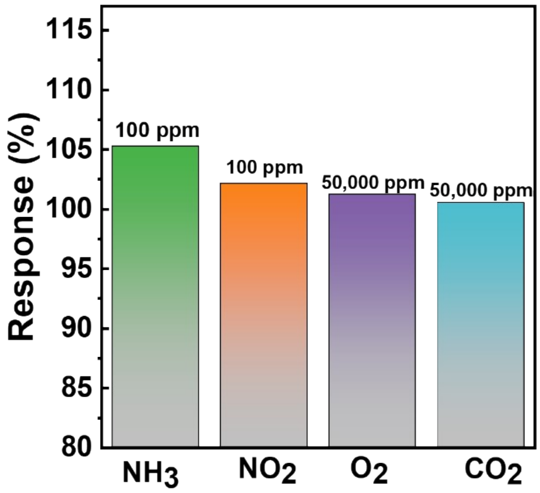

Fig. S6 Response as a function of different gases for the GnP sensor.

Fig. S6 Shows response as a function of different target gases for GnP sensor, under identical operating conditions. NH_3 and NO_2 were tested at 100 ppm, while significantly higher concentrations (50,000 ppm) of CO_2 and O_2 were used, confirming the selective response of the sensor toward NH_3.

Table S1 Reproducibility test of GnP-TiO_2 sensor using ANOVA of regression model.

GnP-TiO_2 Sensor	**No. of cycles**	**Response**	**Mean ± SD**	**Sum of square between groups**	**Mean square between groups**	**Sum of square within groups**	**Mean square within groups**	**F**	**p value**
Sensor 1	1	357.38	349 ± 6.55	519.45	=519.45/2 =259.72 (Degree of freedom = k-1 =3-1 =2)	751.08	=751.08/6 =125.18 (Degree of freedom = N-K =9-3 =6)	2.07	0.206
	2	341.35							
	3	348.44							
Sensor 2	1	348.91	353 ± 10.59						
	2	327.32							
	3	329.34							
Sensor 3	1	351.82	335 ± 9.74						
	2	366.33							
	3	340.47							

Table S2 Stability test of GnP-TiO_2 sensor using T-test.

No.	Response(%) x_i	$(x_i - \grave{x})$	$(x_i - \grave{x})^2$	Mean square= $\frac{\sum(x_i - \grave{x})2}{df}$	Standard error=SD/√n	t value = (Mean - μ/SE)	p=2×(1−F(|t|,df))
1	316.8	-16.66	277.55	= 1830.26/11	12.89928/√12	= 333.46-330.86/3.7237	=F(0.7062,11)≈0.752
2	348.44	14.98	224.40	= 166.38	= 3.7237	= 0.70628	
3	357.38	23.92	572.16				P = 2 x(1-0.752)
4	341.35	7.89	62.25	(df = k-1			= 0.496
5	323.53	-9.93	98.60	= 12-1			
6	330.83	-2.63	6.91	= 11)		(reference value μ = 330.83)	
7	336	2.54	6.45				
8	340.93	7.47	55.80				
9	311.56	-21.9	479.61				
10	336.22	2.76	7.61				
11	327.92	-5.54	30.69				
12	330.59	-2.87	8.23				
			$\sum(x_i - \grave{x})^2$ = 1830.26				

The results showed no statistically significant variation among the repeated measurements (t(11) = 0.706, p = 0.496 > 0.05), indicating good repeatability of the sensing performance during all days.

Table S3 Stability test of GnP sensor using T-test.

No.	Response(%) x_i	$(x_i - \grave{x})$	$(x_i - \grave{x})^2$	Mean square= $\frac{\sum(x_i - \grave{x})2}{df}$	Standard error=SD/√n	t value = (Mean - μ/SE)	p=2×(1−F(|t|,df))
1	103.88	0.24	0.0576	=2.8598/14	0.451964/√15	= 103.64-103.48/0.11669	=F(1.371154,14)≈0.962
2	104.71	1.07	1.1449	= 0.204271	=0.11669	= 1.371154	
3	103.32	0.32	0.1024				P = 2 x(1-0.962)
4	102.54	-1.1	1.21	(df = k-1			= 0.076
5	103.36	-0.28	0.0784	= 15-1			
6	103.68	0.04	0.0016	= 14)		(reference value μ = 103.48)	
7	103.71	0.07	0.0049				

8	103.34	-0.3	0.09				
9	103.65	0.01	0.0001				
10	103.48	-0.16	0.0256				
11	103.92	0.28	0.0784				
12	103.79	0.15	0.0225				
13	103.67	0.03	0.0009				
14	103.83	0.19	0.0361				
15	103.72	0.08	0.0064				
			$\sum(x_i - \grave{x})^2$ = 2.8598				

The results showed no statistically significant variation among the repeated measurements (t(14) = 1.3711, p = 0.076 > 0.05), indicating good repeatability of the sensing performance during all days.