Optimization of graphene-based gas sensors by ultraviolet photoactivation.

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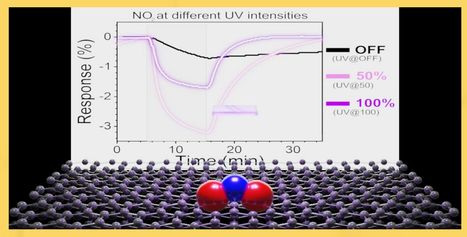
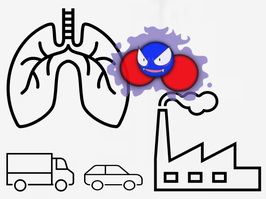


Nitrogen dioxide (NO_2) is an air pollutant derived from human activity that may cause or exhacerbate respiratory complications. We need technologies capable of monitoring NO_2 below toxic level, i.e., sub-ppm range or lower.



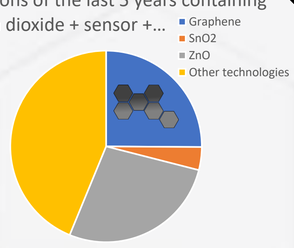
Recommended exposure limits		Estimated lethal concentrations	Typical concentrations in urban areas
Daily	Yearly	(1 hour)	(USA & UK)
0.1-1 ppm	0.02 ppm	174 ppm	0.4-0.5 ppm

Sensors based on the chemiresistive principle, upon analyte exposure the materials electrical properties change, have tipically used metal oxides as actives materials. However, they need to opérate at high temperature which represents a major drawback to their application.

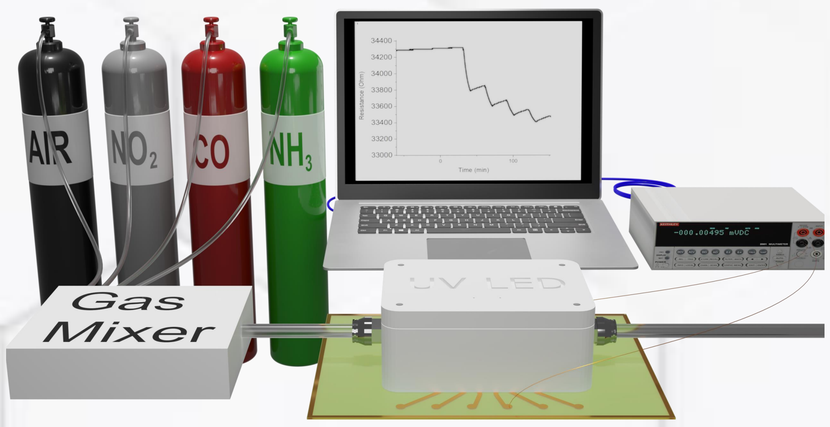
In this context, graphene and other graphene-based materials, with outstanding surface area and high conductivity at room temperature, represent and interesting alternative as active materials.

However, graphene-based gas sensors present poor recovery after the exposure to the analyte,which hinders their potential applications in real life conditions.

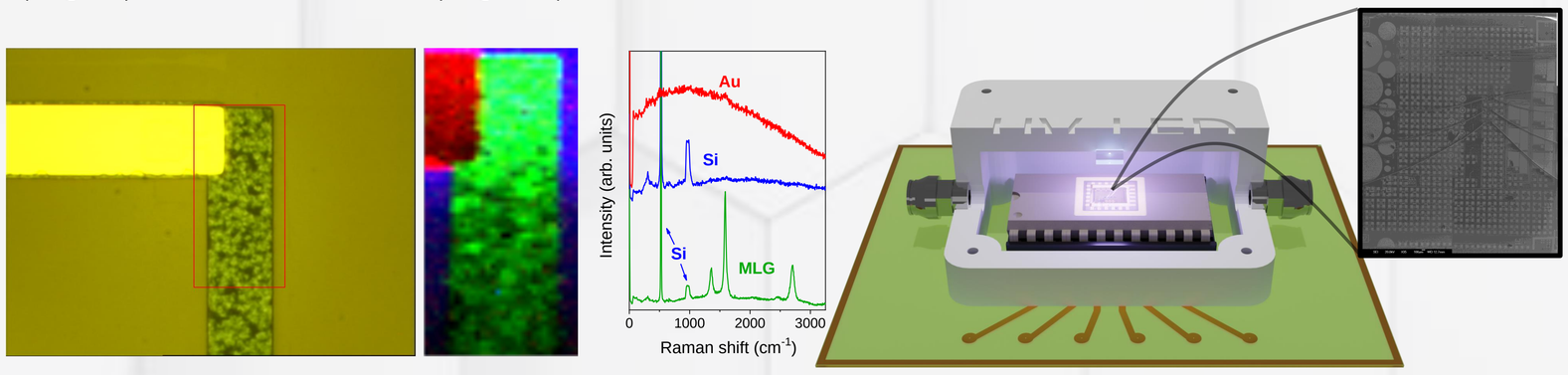
Publications of the last 5 years containing Nitrogen dioxide + sensor +...

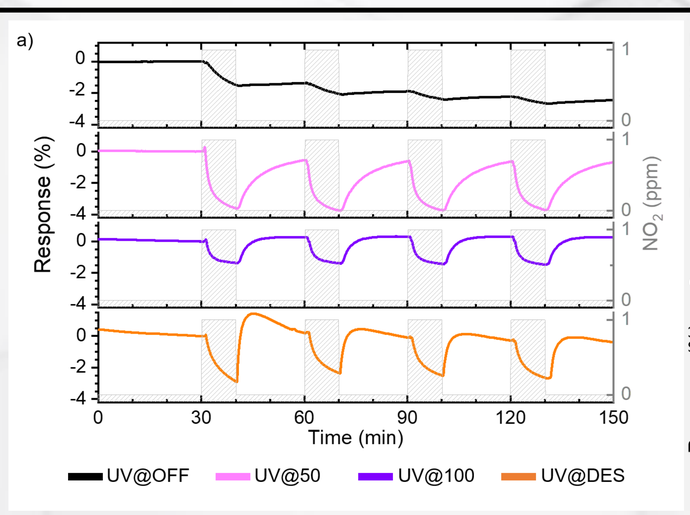


In this work we show how the use of UV irradiation can overcome this problem, increase sensitivity and achieve a limit of detection below the toxicity levels. Interestingly, UV does not damage the material.



The active material used in the device was multi-layer graphene (MLG) grown with CVD over a silicon wafer using a transfer-free method. Gold contacts were then sputtered and wire bonded to build the device electronics.
The MLG presented a low defects ratio (Raman I(D)/I(G) ratio of 0.266) and surface roughness of (AFM). The device presented ohmic resistance (I-V curves).
We tested the device towards NO2/ Air – 1 ppm, CO/ Air – 10 ppm and NH3/ Air – 10 ppm using a 275 nm LED as a UV source. The device operated under continuous UV irradiation (UV@100, 68 W/m^2 and UV@50, 34 W/m^2), under UV irradiation during the purge phase only (UV@DES) and under no UV irradiation (UV@DARK)





The use of UV significantly increased the response and promoted full recovery, i.e., when the sensor was not exposed to the analyte it recovers its initial conditions, greatly enhancing reproducibility.

The effect of UV irradiation on the performance of graphene-based gas sensors can be explained through two main mechanisms that occur simultaneously: The photogeneration of electron-hole pairs and the photodesorption of contaminants, often referred to as in-situ cleaning.
The incident photons create photogenerated electron-hole pairs. For graphene, the photogeneration is caused by absorption in the 275 nm wavelength, related to π-π* electron promotion, according to the following relation:

$$hv \rightarrow e^-_{(hv)} + h^+_{(hv)}$$

The photogenerated charge carriers can then interact with adsorbed molecules, such as water and oxygen species, both electron donors, and cause photodesorption:

$$h^+_{(hv)} + O^-_{2(ads)} \rightarrow O_{2(gas)}$$

Since the experiments used air as a carrier, the photogenerated electron can promote the additional adsorption of oxygen, leading to highly reactive photoinduced oxygen ions:

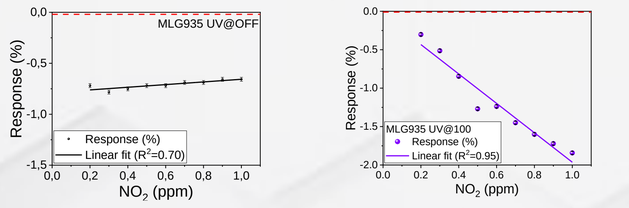
$$O_{2(gas)} + e^-_{(hv)} \rightarrow O^-_{2(hv)}$$

These reactive ions can act as binding sites for the analytes with higher affinity to graphene, like NO_2:

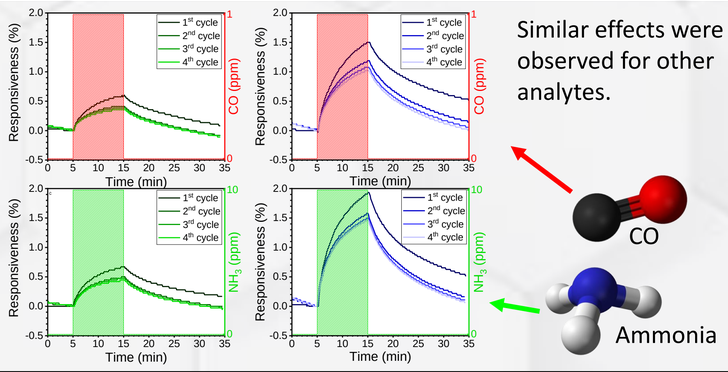
$$2NO_{2(gas)} + O^-_{2(hv)} + e^-_{(hv)} \rightarrow 2NO^-_{2(ads)} + O_{2(gas)}$$

Meanwhile, the adsorption mechanisms that operate no irradiation conditions, i.e., the charge transfer from analytes, still occurs under UV irradiation but are further promoted by the excess of charge carriers from the photogeneration process.

Without UV, the partial recovery causes a non-linear response to different NO_2 concentrations. Therefore, the limit of detection can only be calculated when the device operates under UV irradiation.



$$LoD_{(RMSnoise,\text{Sensitivity})} = \frac{3 * RMSnoise}{Sensitivity} = \mathbf{0.30\ ppb}$$



Similar effects were observed for other analytes.

To sum up, using UV irradiation we get:

- Higher response
- Full recovery after exposure
- Increased reproducibility
- Low limit of detection
- No permanent damages

In essence, we turn the graphene-based gas sensor into something usable under practical conditions for air pollution monitoring.

Material	Main approach	Analyte	Response	Effect of UV/ Other (If no UV)	DOI
rGO		NO_2/ N_2 5 ppm	13%	-	10.1021/nn800593m
		NH_3/ N_2 5 ppm	2.5%		
CNT	Continuous UV: 253.7 nm, 1.7 mW/cm^2	NO/ Air 200 ppm	36%	5-fold increase but reduced lifetime under UV and material removal.	10.1038/srep00343
Mechanical exfoliated graphene	Pristine	NO_2/ N_2 100 ppm	11%	Sensor achieved full recovery under UV with neglectable side effects.	10.1016/j.cartre.2021.10
	Defective graphene (I(d)/I(g)= 0.24)	NO_2/ N_2 100 ppm	32%		
	Defective graphene (I(d)/I(g)= 0.59)	NO_2/ N_2 100 ppm	18%		
Graphite		**NO_2/ Air 0.5 ppm**	**3.32%**		
Ball-milled graphene		**NO_2/ Air 0.5 ppm**	**14.52%**	**Slight improve in response and recovery under UV**	**10.1016/j.snb.2021.129657**
	Continuous UV: 275 nm	**NO_2/ Air 0.5 ppm**	**15.97%**		
CVD-graphene		CO/ Air 100 ppm	3%	-	10.1021/jp100343d
		NO_2/ Air 100 ppm	18%		
CVD-graphene	High temperature operation (150°C)	NH_3/ Air 65 ppm	2.1%	-	10.1016/j.msec.2011.05.008
CVD-graphene	Heat (200°C) and vacuum to force desorption	NO_2/ Air 10 ppm	15%	-	10.1063/1.4720074
		NH_3/ Air 10 ppm	17.5%		
CVD-graphene	Pristine	NO_2/ Air 100 ppm	9.6%	-	10.1039/c6cp07654h
	Defective graphene (I(d)/I(g)= 0.04)		15%		
	Defective graphene (I(d)/I(g)= 0.12)		20%		
	Defective graphene (I(d)/I(g)= 0.38)		13.3%		
	Defective graphene (I(d)/I(g)= 1)		7.8%		
CVD-graphene	Pristine	NO_2/ He 200 ppm	40%	-	10.1016/j.snb.2012.02.036
		NH_3/ He 200 ppm	3.5%		
	Defective graphene (I(d)/I(g)= 0.1-1.1)	NO_2/ He 200 ppm	53%		
		NH_3/ He 200 ppm	25%		
Commercial graphene substrate	Pristine	NO_2/ Air 5 ppm	9.75%	Continuous high-temperature operation 150°C was used to improve recovery	10.1088/0957-4484/23/50/505501
	Defective graphene (I(d)/I(g)= 0.065)	NO_2/ Air 5 ppm	9.1%		
CVD-graphene on a flex. substrate	Recovery under UV: 254 nm, 2.5 mW/cm^2	NO_2/ Air 2.5 ppm	65%	Sensor achieved full recovery under UV without damages.	10.1021/am5084122
CVD-graphene	Continuous UV: 370 nm	NH_3/ N_2 0.6 ppm	1.89%	10-fold increase	10.1016/j.vacuum.2016.08.006
CVD-graphene	Continuous UV: 253.7 nm, 1.7 mW/cm^2	NO_2/ N_2 0.4 ppb	3.6%	UV significantly lowered the LoD with neglectable side effects.	10.1063/1.4742327
		NH_3/ Ar 2 ppb	1.4%		
CVD-graphene	Continuous UV: 265 nm, 1.68 mW/cm^2	NO_2/ Air 100 ppm	26%	7-fold increase	10.1021/acsomega.9b00935
		NH_3/ Air 100 ppm	1.6%	3-fold increase	
		CO/ Air 100 ppm	1.2%	6-fold increase	
CVD-graphene	**Continuous UV: 275 nm, 3.4 mW/cm^2**	**NO_2/ Air 1 ppm**	**3.1%**	**5-fold increase**	**This work (soon to be published)**
	Continuous UV: 275 nm, 6.8 mW/cm^2		**1.7%**	**3-fold increase**	
	Continuous UV: 275 nm, 3.4 mW/cm^2	**CO/ Air 10 ppm**	**1.2**	**3-fold increase**	
		NH_3/ Air 10 ppm	**1.7**	**3-fold increase**	

Different approaches have been considered to improve the performance of graphene-based gas sensors, the most common are:

- Material selection
- **Techniques to increase the active surface**
- **Defects engineering**
- **Use of UV irradiation**

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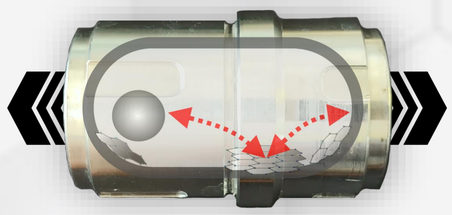
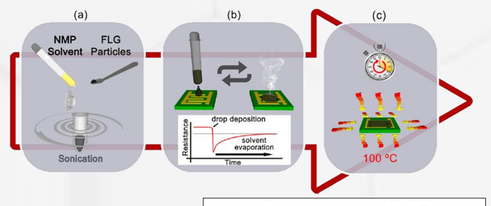
- Use of high temperatures
- Functionalization with nanoparticles (metals or metal oxides)

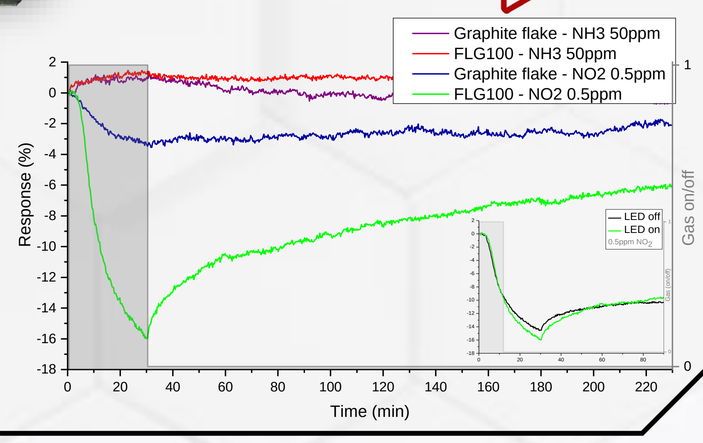




*In a recent work, we used UV on a ball-milled graphene-based material.

Due to its mesoporosity and 3D structure, we obtained high response, but the effect of UV was low. An interesting experiment to contrast with the one using CVD Graphene.

We obtained an NO_2 LoD as low as 25 ppb.



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