

# Graphene Nanoribbons-Based Ultra-Sensitive Chemical Detectors

## Supporting Information

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### Calculation of the Gas Phase Concentration from the Contaminant Surface Density

In this section we elaborate on our device sensitivity analysis using the Langmuir adsorption isotherm, [1-3] as presented in formula (2) of the main text, to evaluate the contaminants' air concentrations from their threshold surface densities. As mentioned in the main text, the Langmuir adsorption isotherm, relating the contaminant surface density  $\Gamma$  to its gas phase number density  $n$ , is given by:

$$\frac{\Gamma}{\Gamma_{\max}} = \frac{n}{n + n_{\max} \cdot \exp(-E_{\text{ads}}/k_{\text{B}}T)}, \quad (\text{A.1})$$

where  $\Gamma_{\max}$  is the largest possible contaminant surface density,  $n_{\max}$  is the highest contaminant number density that can be attained in gas phase,  $E_{\text{ads}}$  is the binding energy of the contaminant molecule to the surface,  $T$  is the temperature, and  $k_{\text{B}}$  is Boltzmann's constant.

Isolating the air number density we obtain:

$$n = \left( \frac{\Gamma}{\Gamma_{\max} - \Gamma} \right) n_{\max} \cdot \exp(-E_{\text{ads}}/k_{\text{B}}T) \quad (\text{A.2})$$

For  $\Gamma$  we use the value of the minimal detectable surface contaminant densities of  $\Gamma = \frac{1}{4.3}$ ,  $\frac{1}{18.9}$ , and  $\frac{1}{16.9} \left[ \frac{\text{molecules}}{\text{nm}^2} \right]$ , for the 22x7, 76x9, and 56x11 systems, respectively. These values correspond to a cross-correlation factor of  $r \gtrsim 0.98$  between the I-V curves of the bare-Li and Bz-Li systems (see Fig. 4 and relevant discussion in the main text). Accordingly,  $\Gamma_{\max} = \frac{1}{2.4}$ ,  $\frac{1}{3.0}$ , and  $\frac{1}{3.6} \left[ \frac{\text{molecules}}{\text{nm}^2} \right]$  correspond to the highest density of lithium sites that allow for benzene anchoring with no apparent steric hindrance and inter-site electronic reciprocity.  $n_{\max}$  can be estimated as the inverse van der Waals volume of the benzene molecule. To this end, we approximate this volume by a sphere of radius of 0.34 nm [4] such that  $n_{\max} = \frac{1}{V_{\text{vdW-Benzene}}} =$

$\frac{1}{\frac{4\pi R^3}{3} R_{vdW-Benzene}} = \frac{3}{4\pi \cdot 0.34^3} \left[ \frac{\text{molecules}}{\text{nm}^3} \right] = 6.1 \frac{\text{molecules}}{\text{nm}^3}$ . The binding energies of benzene on the lithium anchoring sites are obtained as total energy differences by first fully relaxing the benzene-lithium doped systems with periodic boundary conditions along the lead axis followed by increasing the perpendicular benzene-nanoribbon distance with fixed lithium position until no significant energy modifications are recorded. The obtain values are 0.98, 1.17, and 1.14 eV, for the 18x7, 18x9, and 18x11 systems, respectively. At room temperature (298 K) the thermal energy is given by  $k_B T = 0.02568 \text{ eV}$ . With this we have for the 22x7 system:

$$n_{Bz} = \left( \frac{\frac{1}{4.3} \left[ \frac{\text{molecules}}{\text{nm}^2} \right]}{\frac{1}{2.4} \left[ \frac{\text{molecules}}{\text{nm}^2} \right] - \frac{1}{4.3} \left[ \frac{\text{molecules}}{\text{nm}^2} \right]} \right) 6.1 \left[ \frac{\text{molecules}}{\text{nm}^3} \right] \cdot \exp(-0.98 [\text{eV}]/0.02568 [\text{eV}])$$

$$\approx 2 \times 10^{-16} \left[ \frac{\text{molecules}}{\text{nm}^3} \right].$$

Given the dry air number density of  $n_{\text{air}} = 0.02504 \left[ \frac{\text{molecules}}{\text{nm}^3} \right]$  and since under standard temperature and pressure the mole ratio of a gas is identical to its volume ratio we have:

$$\frac{n}{n_{\text{air}}} = \frac{2 \times 10^{-16} \left[ \frac{\text{Benzene molecules}}{\text{nm}^3} \right]}{0.02504 \left[ \frac{\text{air molecules}}{\text{nm}^3} \right]} \approx 8 \times 10^{-15} \approx 10^{-5} \text{ ppbv}$$

Similarly, for the 76x9 and 56x11 systems we obtain  $\sim 10^{-9}$  ppbv, and for the physisorbed benzene molecule ( $E_{\text{ads}} \approx 0.5 \text{ eV}$ ) [5-7] we obtain a detection air concentration threshold of the order of 0.1-1 ppmv depending on the threshold and maximal surface densities considered. We note that our estimations for the threshold detectable contaminant air concentrations are extremely sensitive toward the calculated chemisorption energy and can vary by two orders of magnitude with binding energy variations of 10%. Hence, one should regard them as crude estimates for the expected detection thresholds.

## Zero Point Energy Calculation

Since the calculated air concentration is very sensitive to the value of the binding energy it is important to evaluate the zero point energy (ZPE) and compare it with the overall benzene binding energy on lithium anchoring sites at the surface of graphene ( $\sim 1$  eV). We evaluate the ZPE by fitting the binding energy curves with a harmonic term near the potential well minimum and extracting the corresponding frequency (See Fig. S1). To reduce computational burden, we use finite model systems in these calculations where the edges of the periodic unit cells depicted in Fig. 1 of the main text are passivated with hydrogen atoms. By direct comparison to full PBC calculations on some sample points along the binding energy curves we estimate the calculated binding energy to be modified by less than 10% due to this choice. The corresponding spring constants that we obtain for the three AGNRs considered systems are  $K \cong 1.7 - 2.7 \left[ \frac{eV}{\text{\AA}^2} \right]$ . Considering the fact that the mass of the Li-adsorbed nanoribbon is significantly higher than that of a benzene molecule, we can assume that the reduced mass approximately equals that of the benzene adsorbate:

$$\mu = \frac{(m_{benzene}) \cdot (m_{Li-graphene})}{(m_{benzene}) + (m_{Li-graphene})} \approx m_{benzene}$$

Hence, the largest corresponding frequency of the harmonic oscillator is given by:

$$\begin{aligned} \omega &= \sqrt{\frac{K}{\mu}} = \sqrt{\frac{K}{m_{(benzene)}}} = \sqrt{\frac{2.7[eV/\text{\AA}^2]}{\frac{78.11184}{1000} [kg/mol]}} = \sqrt{\frac{2.7 \times 10^{20}[eV/m^2]}{\frac{78.11184}{1000} [kg/mol]}} \\ &= \sqrt{\frac{2.7 \times 10^{20}[eV/m^2] \cdot 1.602 \times 10^{-19}[J/eV]}{\frac{78.11184}{1000} [kg/mol]}} \\ &= \sqrt{\frac{43.254 [kg/sec^2]}{\frac{78.11184}{6.022 \times 10^{26}} [kg/molecule]}} = \sqrt{3.335 \times 10^{26} \left[ \frac{1}{sec^2} \right]} \\ &= 1.83 \times 10^{13} \left[ \frac{1}{sec} \right]. \end{aligned}$$

The corresponding ZPE is:

$$E_0 = \frac{1}{2} \hbar \omega = \frac{1}{2} \cdot 6.582 \times 10^{-16} [eV \cdot sec] \cdot 1.83 \times 10^{13} \left[ \frac{1}{sec} \right] = 0.006 [eV],$$

which can clearly be neglected with respect to the overall binding energy of  $\sim 1$  eV when performing the air concentrations calculations presented above. We note that due to the shallowness of the binding energy curve of the 18x11 system we could not obtain a clean parabolic fit in this case. Nevertheless, since the zero point energies are estimated to be three orders of magnitudes smaller than the overall binding energies a rough estimation is sufficient.

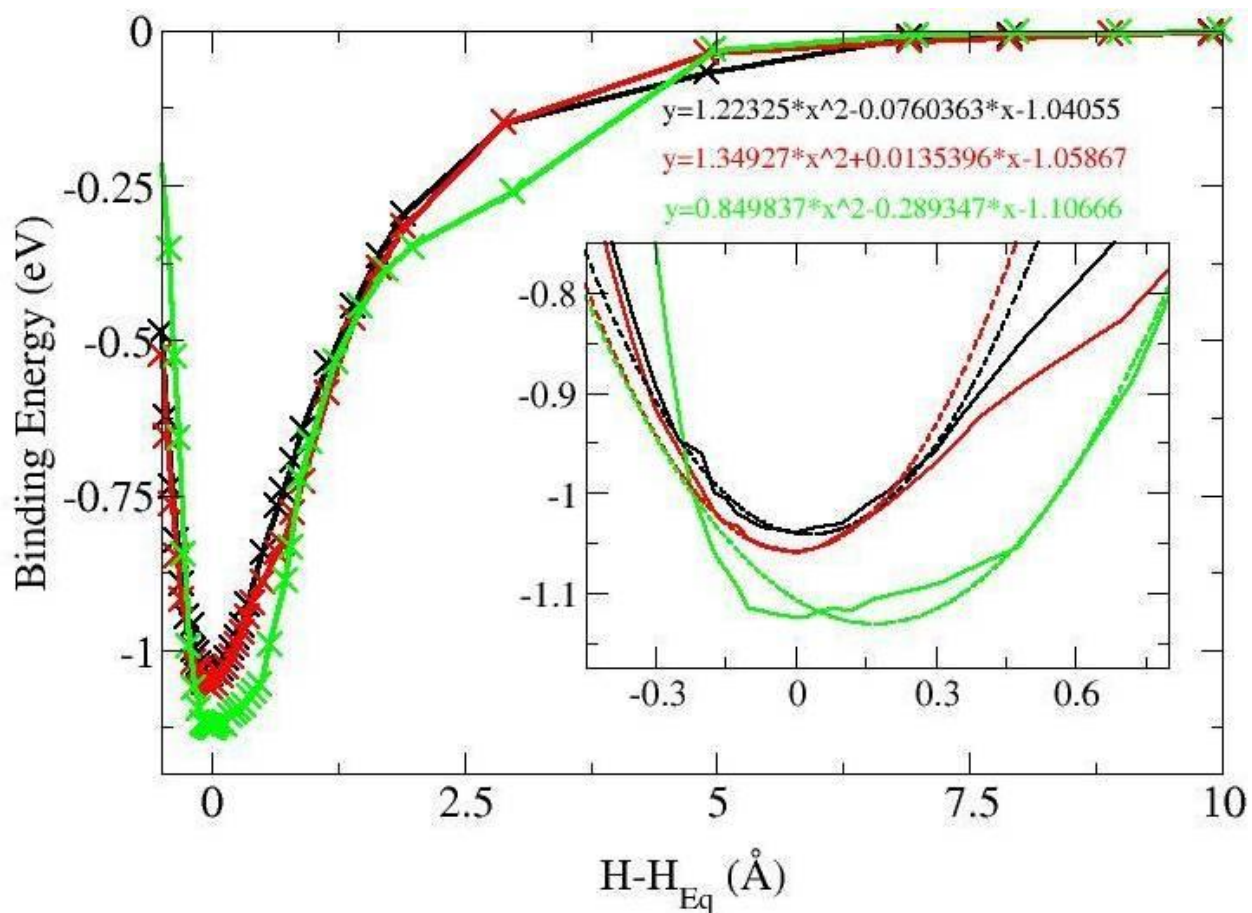


Figure S1: Binding energy of a benzene molecule on the Li-adsorbed finite hydrogen passivated 18x7 (full black line), 18x9 (full red line) and 18x11 (full green line) systems calculated at the HSE/6-31G\*\* level of theory. A parabolic fit was made to each curve (see inset) in order to extract the spring constant.

## References:

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