

## Supplementary Information

# Understanding Gas Adsorption in MOF-5/Graphene Oxide Composite Material

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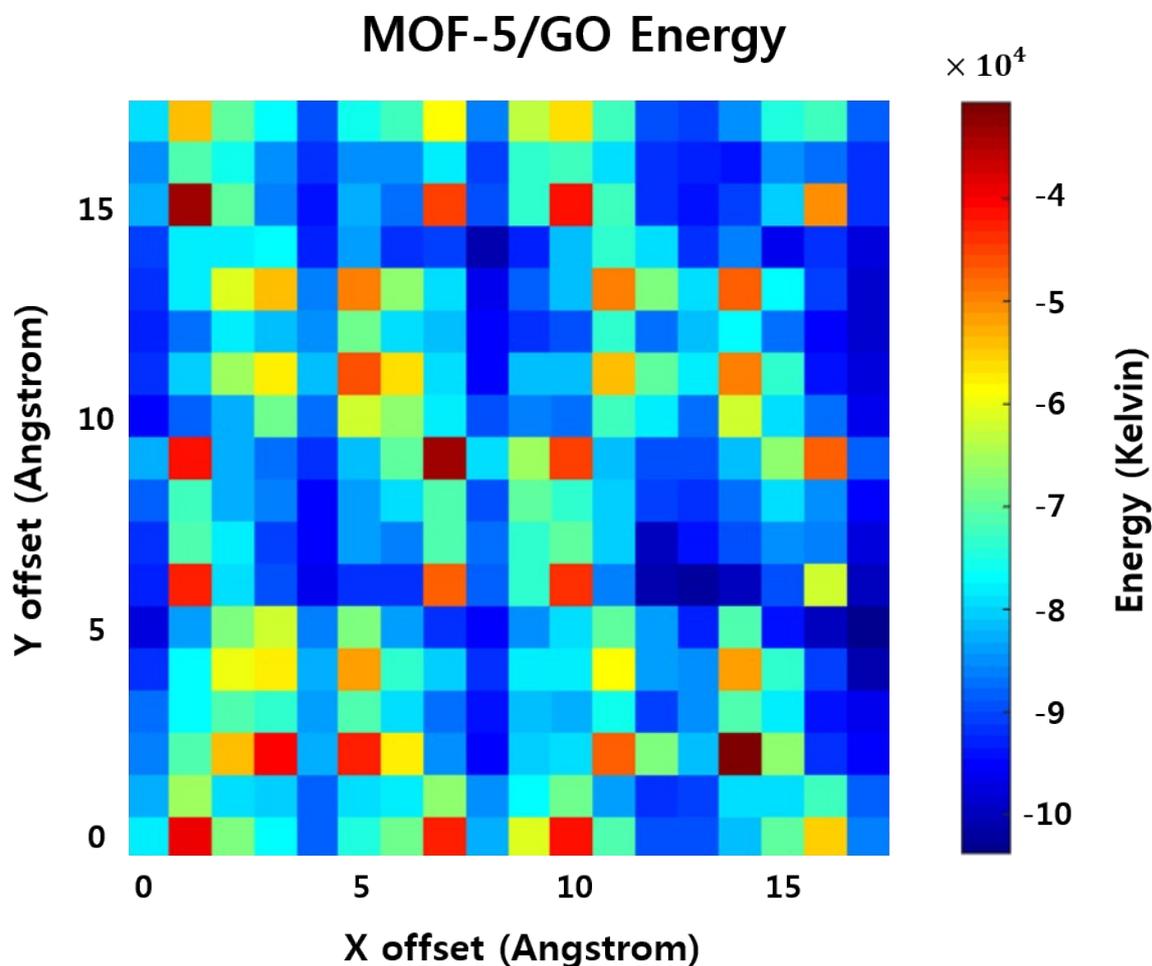
## **Simulation methods**

**Henry's constant ( $K_H$ ) calculations:**  $K_H$  were computed using Widom particle insertion Monte Carlo moves. In all of our simulations, we used the graphics processing units (GPU) code<sup>1</sup> that enabled significant amount of speedup compared to a conventional CPU code. The three-dimensional energy grid with size  $0.15 \times 0.15 \times 0.18 \text{ \AA}^3$  were constructed. The Z-dimensional mesh size is  $0.03 \text{ \AA}$  larger than both the X and the Y directions due to the memory constraints within the GPU DRAM.

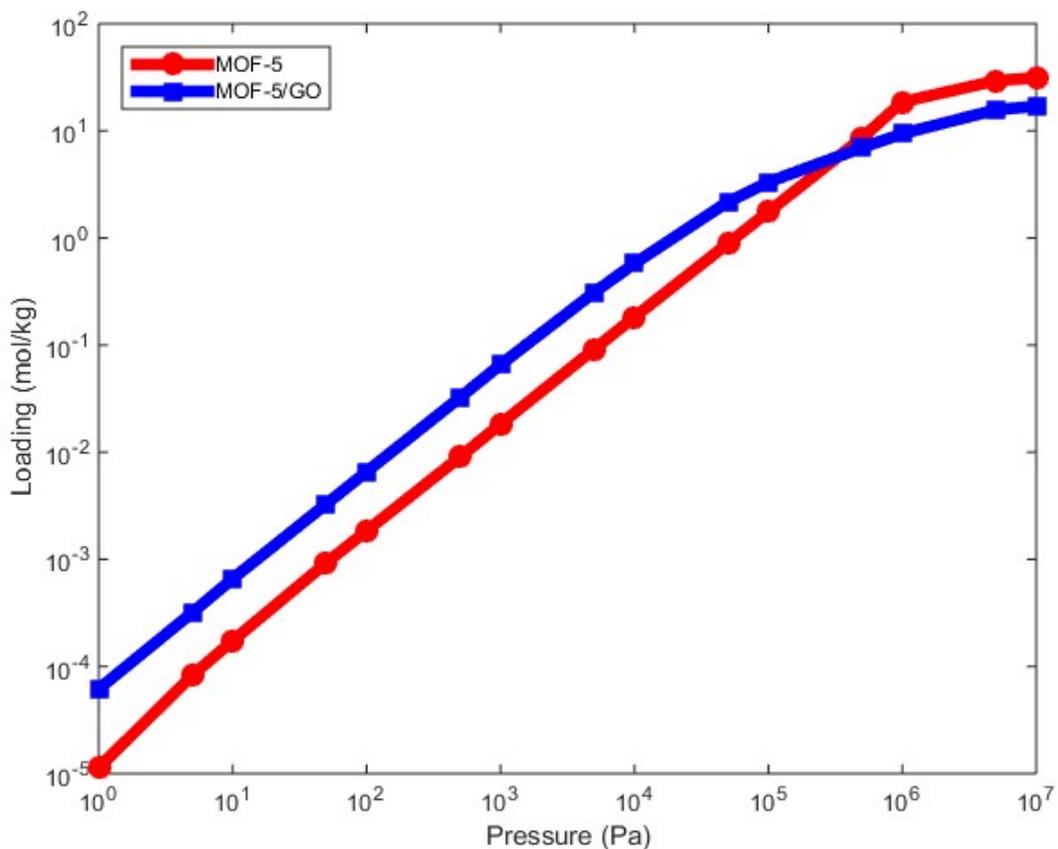
**Graphene Oxide (GO) structure preparations:** Several steps were carried out in this study to prepare GO structures. First, initial GO structures were prepared by randomly placing functional groups (i.e., epoxy and hydroxyl) on both sides of a pristine graphene that has a dimension of approximately  $18 \text{ \AA}$  by  $18 \text{ \AA}$  (i.e., X-Y plane, while the Z-direction is perpendicular to the GO plane). The GO structure considered in this study possesses an epoxy: hydroxyl ratio of 1:1 and a total oxygen concentration of 25%. Initial GO structures were then preliminarily relaxed via energy minimization implemented in LAMMPS<sup>2</sup> using reactive force field (ReaxFF).<sup>3</sup> Subsequently, full geometry relaxation, including lattice vectors along the X and Y directions, was then carried out using density functional theory (DFT) implemented in Quantum ESPRESSO.<sup>4</sup> In DFT calculations, Troullier-Martins type norm-conserving pseudopotentials were adopted with a kinetic energy cutoff of 80 Rydberg and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used. The structures were relaxed until each component of the residence forces on each atom is less than  $0.001 \text{ Rydberg/Bohr}$  while the lattice vectors were optimized until stress

tensor components are smaller than 0.5 kbar. A  $\Gamma$ -centered 1x1x1 k-point sampling was utilized. We note that, in our calculations, a vacuum distance of 18 Å along the Z-direction was used to avoid self-interactions between GO sheets. For the determination of GO-GO inter-planar distances, dispersion forces between layers are anticipated to be critical. Accordingly, DFT calculations with vdW-DF2 exchange-correlation functional<sup>5</sup> were used.

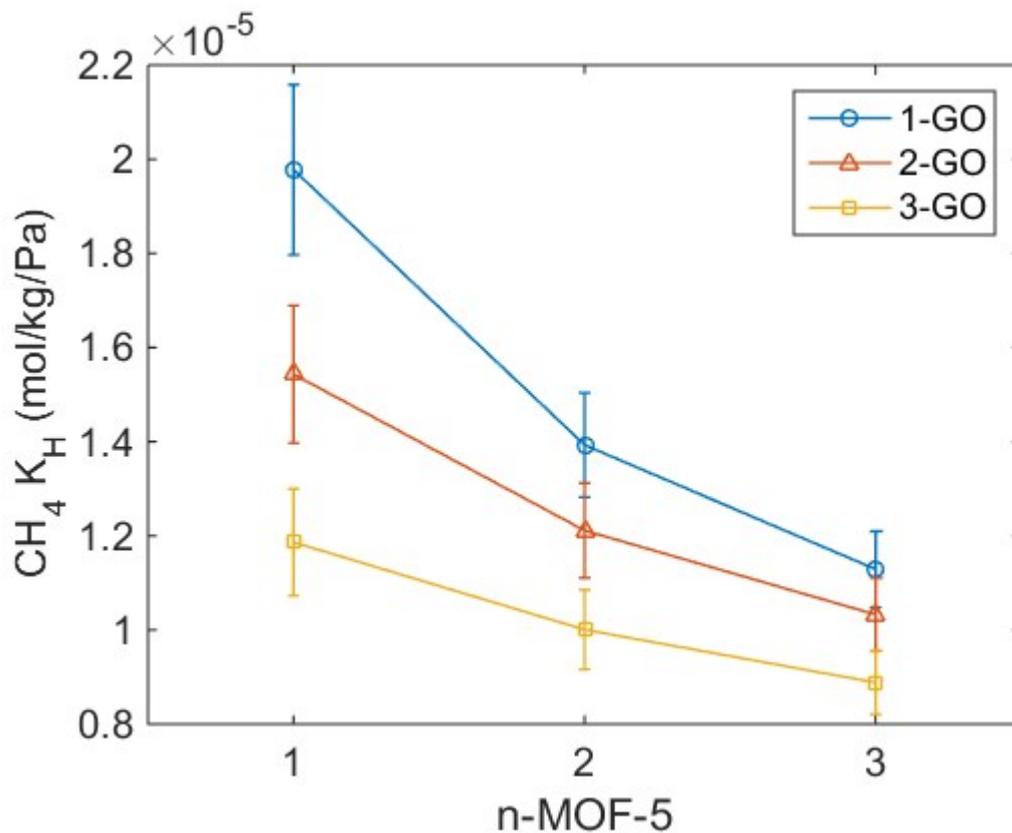
## Additional Figures



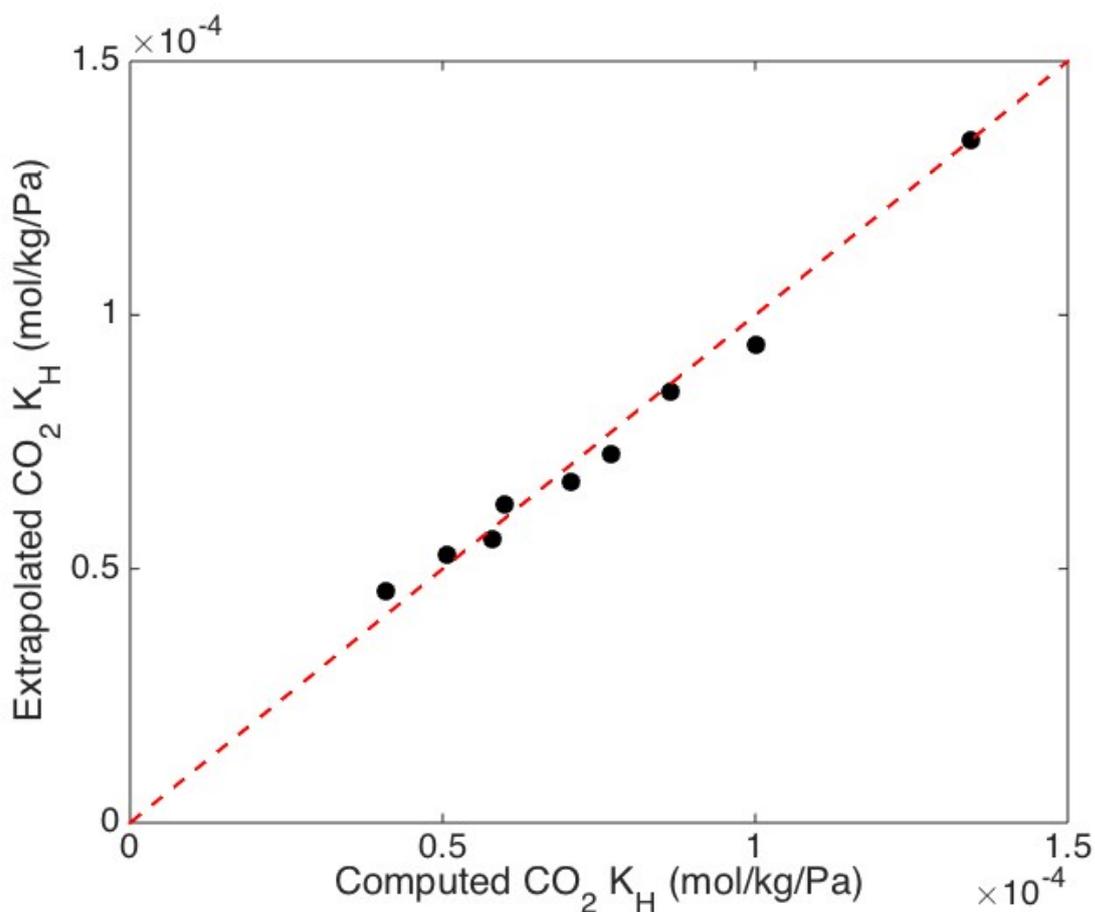
**Figure S1 MOF-5/GO Potential Energy Contour.** MOF-5/GO potential energies were obtained for various different X and Y offsets (for a given optimal X distance) where MOF-5 was kept stationary and the GO plane was moved along the X-Y plane which is parallel to the MOF-5/GO interface plane. The dark blue denotes lowest energies and we took five “diverse” X, Y offset positions as the minimum energy structures for our analysis.



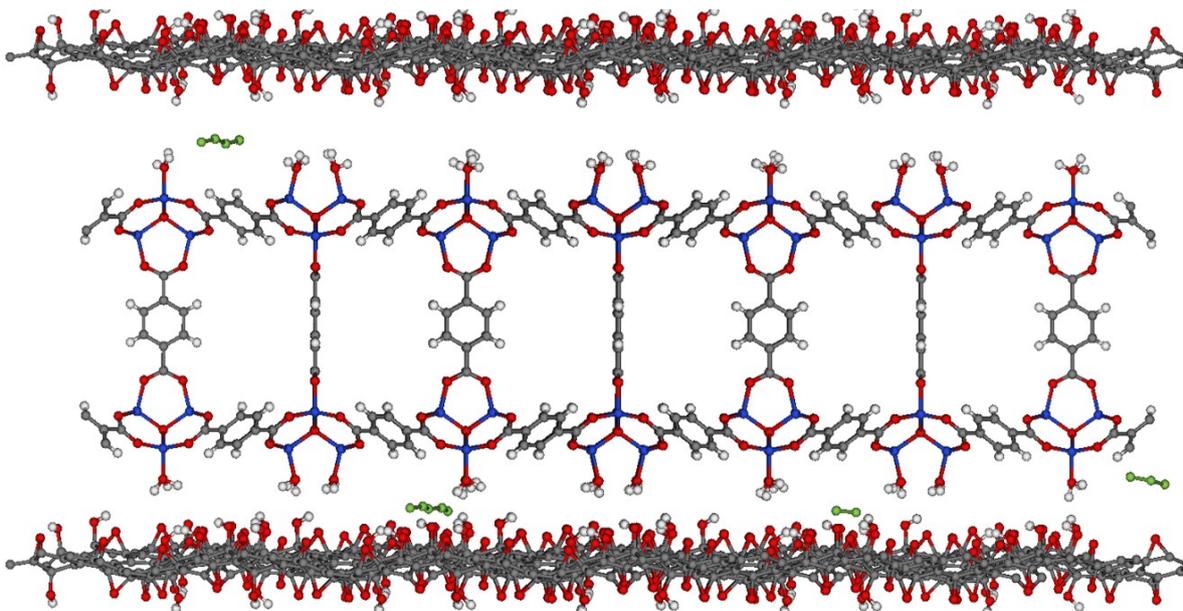
**Figure S2** CO<sub>2</sub> adsorption isotherm data for MOF-5 and 1MOF-5/1GO. The adsorption isotherm data is computed at T = 298 K and shows that uptake for MOF-5/GO > MOF-5 at lower pressures (stronger binding sites) while uptake for MOF-5/GO < MOF-5 at higher pressures (reduction of pore volume).



**Figure S3 CH<sub>4</sub> K<sub>H</sub> versus n-MOF-5/m-GO.** Similar to the case for CO<sub>2</sub> K<sub>H</sub> versus n-MOF-5/m-GO, the Henry's constant decreases upon adding more layers of either MOF-5 or GO as the proportional volume of the MOF-5/GO interface decreases for both cases.



**Figure S4 Computed versus Extrapolated  $\text{CO}_2 K_H$  for n-MOF-5/m-GO.** Given the computational constraints put forth to obtain accurate  $K_H$  for a 1000 supercell MOF-5/GO material, we use Equation (1) as shown in the article to obtain an approximate value of  $K_H$ . The validity of the mathematical expression is tested against computed  $\text{CO}_2 K_H$  values for  $n = 1, 2, 3$  and  $m = 1, 2, 3$ , n-MOF-5/m-GO structures. The two sets of data show good agreement as the nine data points lie close to the dashed red segment.



**Figure S5 Minimum Energy Configurations of Linear Alkanes in MOF-5/GO.**

The image is captured from the last configuration of 1 million cycle Monte Carlo simulation. The color represents carbon in MOF-5/GO (black), oxygen (red), hydrogen (white), zinc (blue), and carbon in alkanes (green), respectively. Hydrogens in alkanes are excluded in this figure for simple view.

## **References**

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