Supporting Information for:
Molecular Dynamics Study of the Pore Formation in Single Layer Graphene Oxide by Thermal Reducing Process

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1. *Ab initio* molecular dynamics

To verify the accuracy of ReaxFF MD trajectories, hence the applicability of such a force field to model the breaking and formation of bonds in GO at high temperatures, we compared classical results with accurate *ab initio* MD simulations. We considered one low-coverage ($\theta = 10\%$) GO structure, containing only epoxides on the same side of the basal plane, in packed configuration. This sample, with a supercell of $\sim 17 \times 17$ Å and a 12Å-thick vertical vacuum layer between periodic replicas, is smaller than the structures investigated classically due to a much higher computational cost of first principle techniques. These dimensions although, are typical of GO models investigated by mean of DFT [1] [2] [3] and were shown to provide reliable results, with negligible self-interaction between periodic replicas. We only compared results at $2500K$ to reduce the simulation time of the test, being desorption events faster at higher temperatures. We performed accurate Car-Parrinello Molecular Dynamics (CPMD) simulations using cp.x code within the Quantum Espresso 6.3 suite [4]. Electron exchange and correlation

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were approximated using the PBE functional [5], with core-electrons potential replaced by ultrasoft pseudopotentials. Electronic wavefunctions were approximated by planewaves expansion up to a converged energy cutoff of $36 Ry$. After initial system setup and electronic energy minimization, CPMD was performed using an electron fictitious mass $\mu = 200 a.u.$ and a timestep $dt = 6 a.u.$ for Verlet integration of the equations of motion. As with classical dynamics we increased the temperature of our system gradually, from $\sim 0K$ to $2500K$ in $\sim 4ps$. When the system reached thermal equilibrium we performed $16ps$ of microcanonical (NVE) MD during which we collected data for trajectory analysis. Although temperature control was not applied during these $16ps$, the system temperature remained stable $\sim 2500K$ as set initially. The evolution of this sample during this *ab initio* thermal treatment is close to that of similar GO structures treated classically. In particular, from our low-coverage sample containing only epoxide groups, we detected the desorption of 2 CO molecules and 1 CO_2 molecule, in close agreement with results reported in Figure 1 of the main manuscript. Snapshots showing the desorption of CO and CO_2 are reported in Figure S1. We did not observe any O_2 desoprtion, probably due to the low coverage of the sample and the short simulation time.
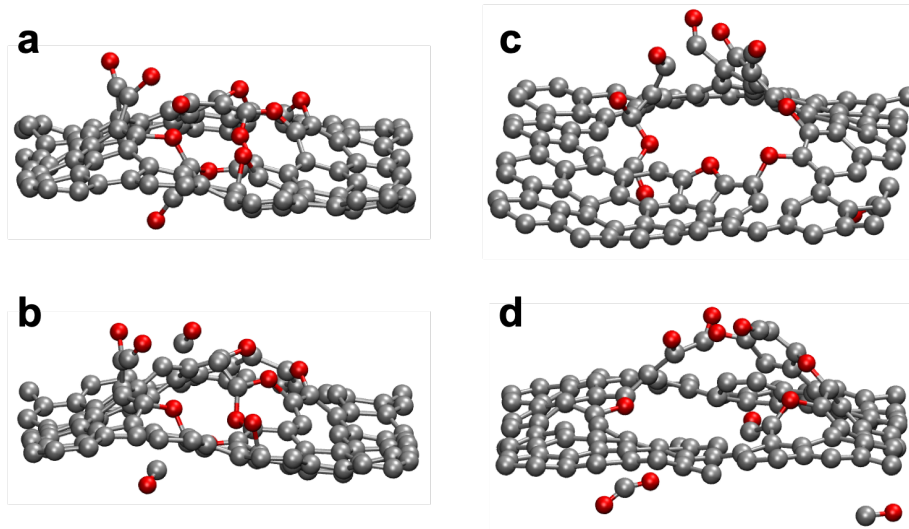

Figure S1: Snapshots showing the desorption of CO and CO_2 from GO during thermal treatment at 2500K. Snapshots a and b show the desorption of CO, while snapshots c and d show the desorption of CO_2.

2. Temperature cycle

The temperature cycle used in the molecular dynamics simulations, representative of a harsh reducing process, is shown in Figure S2. The target temperature indicated in the graph is either 1000 K, 1500 K or 2500 K.
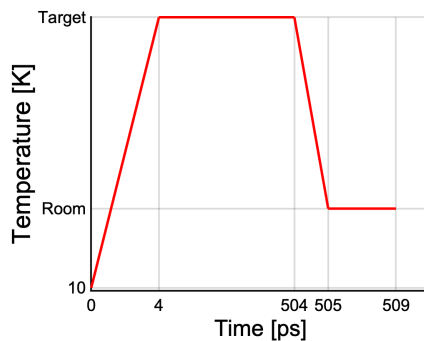

Figure S2: Simulation of the harsh reducing process. Applied temperature over time.

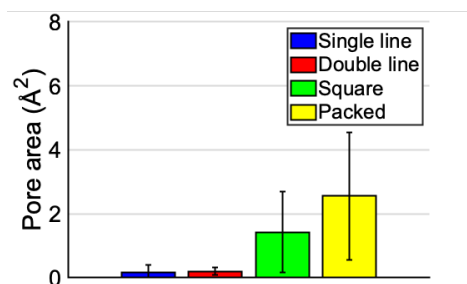## 3. Epoxides distributed on different sides of graphene

Figure S3: Final pore area of the GO cluster illustrated in Figure 3a of the main manuscript having the epoxide functional groups distributed on different sides of the basal plane.

We, here, show how the presence of epoxides on both sides of the basal plane of graphene can affect the final pore area. The calculation was performed on the same structures depicted in Figure 3a of the main manuscript but with epoxide alternated between top and bottom position on the sheet. The final pore area data, shown in Figure S3, are consistent with the ones

obtained for pores having epoxides on the same side. Linear clusters do not lead to the formation of pores suited for salt filtration whereas more circular ones are the most effective, with the packed configuration giving the best results. In Figure S4, the number and types of species that desorb during a harsh temperature process is indicated for both sheets with epoxides on the same side and on different sides. The trend is similar in both cases. In general, CO is the main molecule that desorbs and that causes carbon removal.
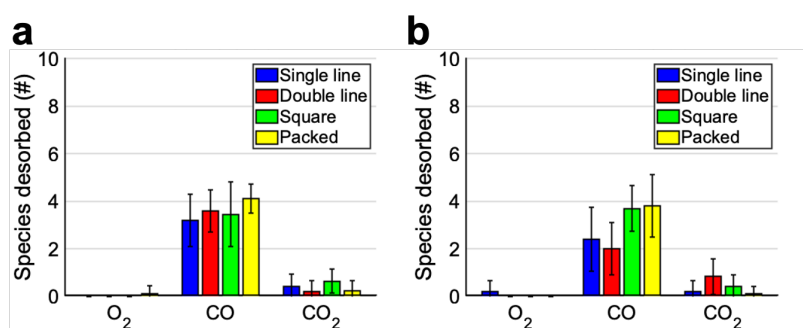

Figure S4: Number and types of species desorbed for sheets with epoxides on the same side (a) and on different sides (b) of the graphene sheet.

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