Supplementary Information: Oxidation vs Agglomeration: Impact of Graphene Oxidation on Self-Interactions and PFAS Capture

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S1: Images of Flakes Under Study

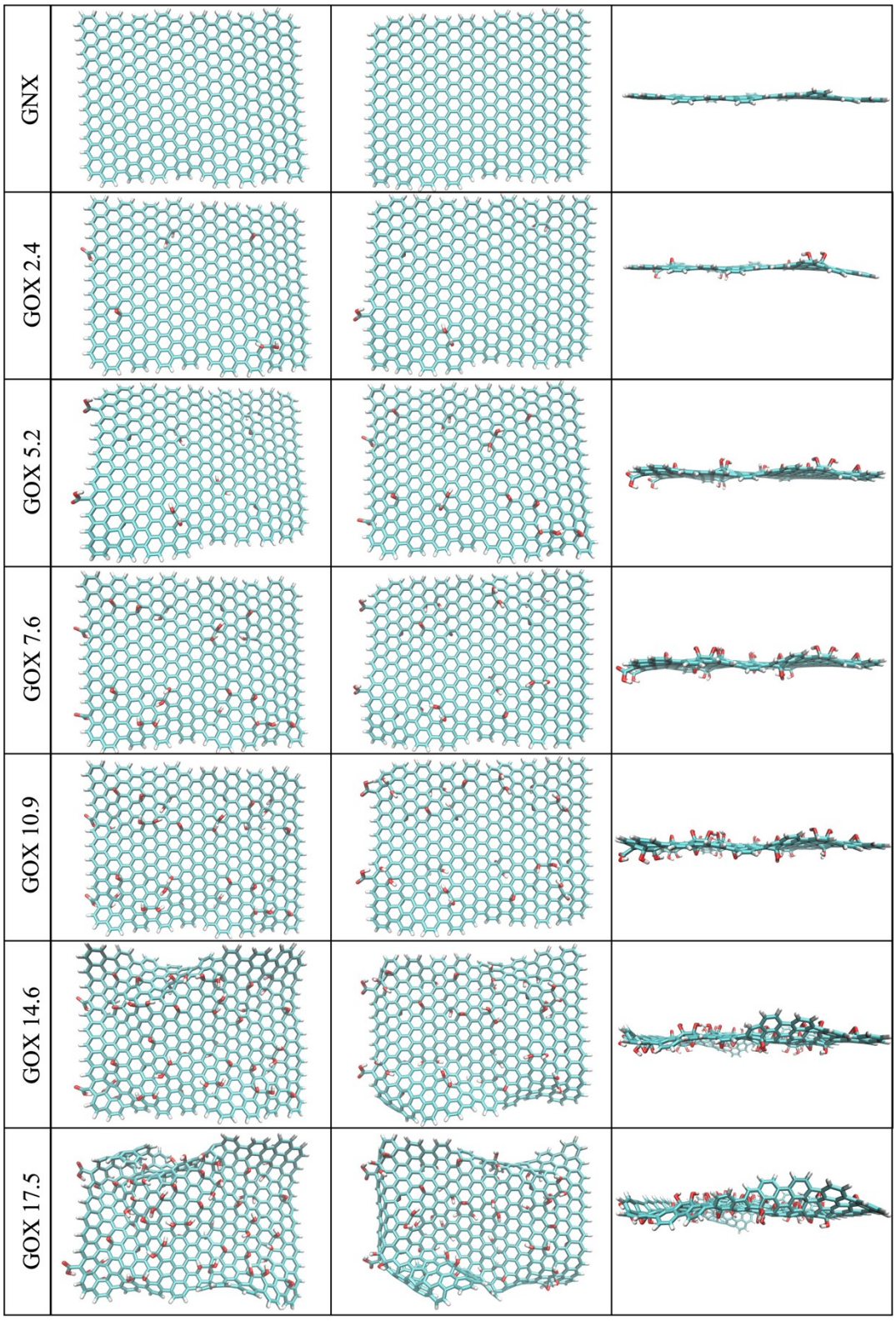

Figure S1: Front, back, and side view of all flakes under study

S2: Number of Functional Groups Present on each Flake

Table 1 lists the number of functional groups present, hydroxyl/epoxy ratio, and C/O ratio of each graphene oxide flake

Flake Name	Hydroxyl	Epoxy	Carboxyl	Hydroxyl/Epoxy ratio	C/O ratio
GNX	0	0	0	-	-
GOX 2.4	4	2	1	2.0	53.6
GOX 5.2	8	6	2	1.3	23.9
GOX 7.6	14	9	2	1.6	15.9
GOX 10.9	24	12	2	2.0	10.8
GOX 14.6	34	18	2	1.9	7.7
GOX 17.5	44	22	2	2.0	6.1

S3: Number of Molecules in Each Simulation

Table S2 lists the number of each type of molecule in the simulation

Flake	Number of PFOA Molecules	Number of PFOS Molecules	Number of PFBA Molecules	Number of Flakes	Number of Sodium Ions	Number of Water Molecules
GNX	5	5	5	5	15	22612
GOX 2.4	5	5	5	5	15	22572
GOX 5.2	5	5	5	5	15	22523
GOX 7.6	5	5	5	5	15	22481
GOX 10.9	5	5	5	5	15	22408
GOX 14.6	5	5	5	5	15	22337
GOX 17.5	5	5	5	5	15	22282

S4: Histogram of Charge Counts Per Flake

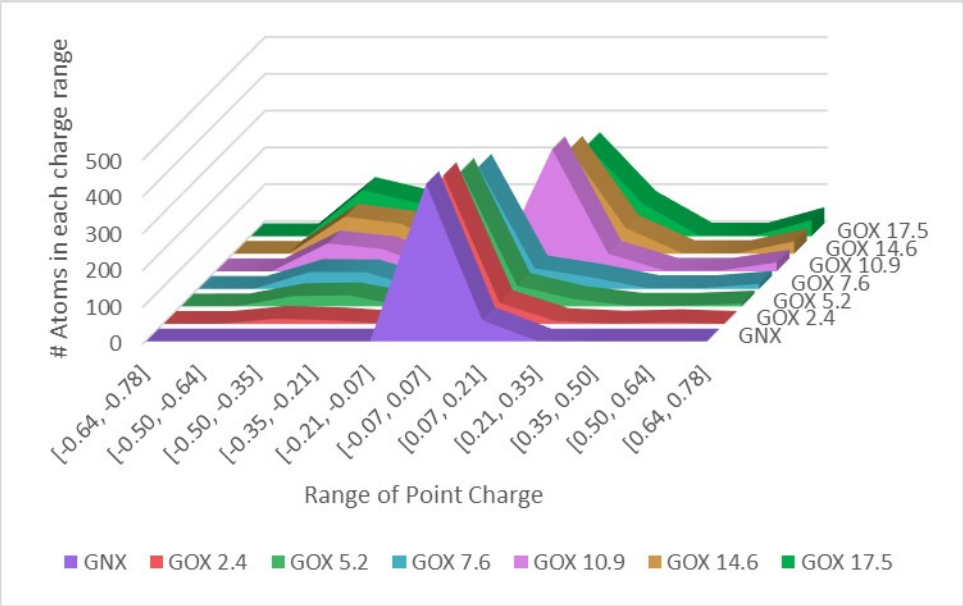

Figure S2: Histogram distribution of atomic point charges counted across all atoms (carbon, oxygen, and hydrogen atoms) per flake.

The charges assigned to every atom of the flake were binned by their partial atomic charge to create the histogram in Figure S2. As oxidation increases, the number of atoms assigned with negative charge from -0.7 to -0.21 increases. The number of neutral atomic charges ranging from [-0.07, 0.07] and slightly positive [0.07, 0.21] decreases. And the higher positive charged species [0.64, 0.78] increase (the carbon connected to the functional groups is positively charged). Of course, these changes in charge towards higher polarity account for the increasing hydrophilicity of the flake as oxidation increases. This trend is well recognized in past computational and experimental literature.[57,68,73,75] The increased polarity includes effects to two phenomena critical to PFAS capture: 1) diminishes the size and number of hydrophobic sites, and 2) yields greater separation of the flakes, thus increases surface area accessible by solvent. These two phenomena are linked and exhibit competing effects; requiring both be in balance for optimal capture to occur.

S5: GOX 7.6 Aggregation without PFAS

To test whether or not the flake aggregation results are not impacted by the initial packing of systems with PFAS, simulations were executed on GOX 7.6 without PFAS. GOX 7.6 was chosen as it has the strongest interaction with the PFAS, the most delicate balance in aggregation, and would be the most likely to be influenced by PFAS if any of these flakes were as examined herein. Twelve unique and random configurations of 5 GOX 7.6 flakes and water were packed using the same methodology as listed in the methods section of the main manuscript, except without PFAS or counter ions. The flake – flake LIE and flake surface area were calculated. The results are shown in Table S3. The surface area and LIE of GO7.6 with and without PFAS are within error of each other. Thus, flake aggregation is not impacted by packing with the PFAS.

Table S3: Flake – flake LIE, and flake surface area for GOX 7.6 simulations with and without PFAS

Calculated Values	With PFAS	Without PFAS
LIE: Flake – Flake (kcal/mol)	-62 ± 22	-68 ± 31
Surface Area ($Å^2$)	14357 ± 717	14861 ± 713

S6: Number of contacts between PFAS and Flakes

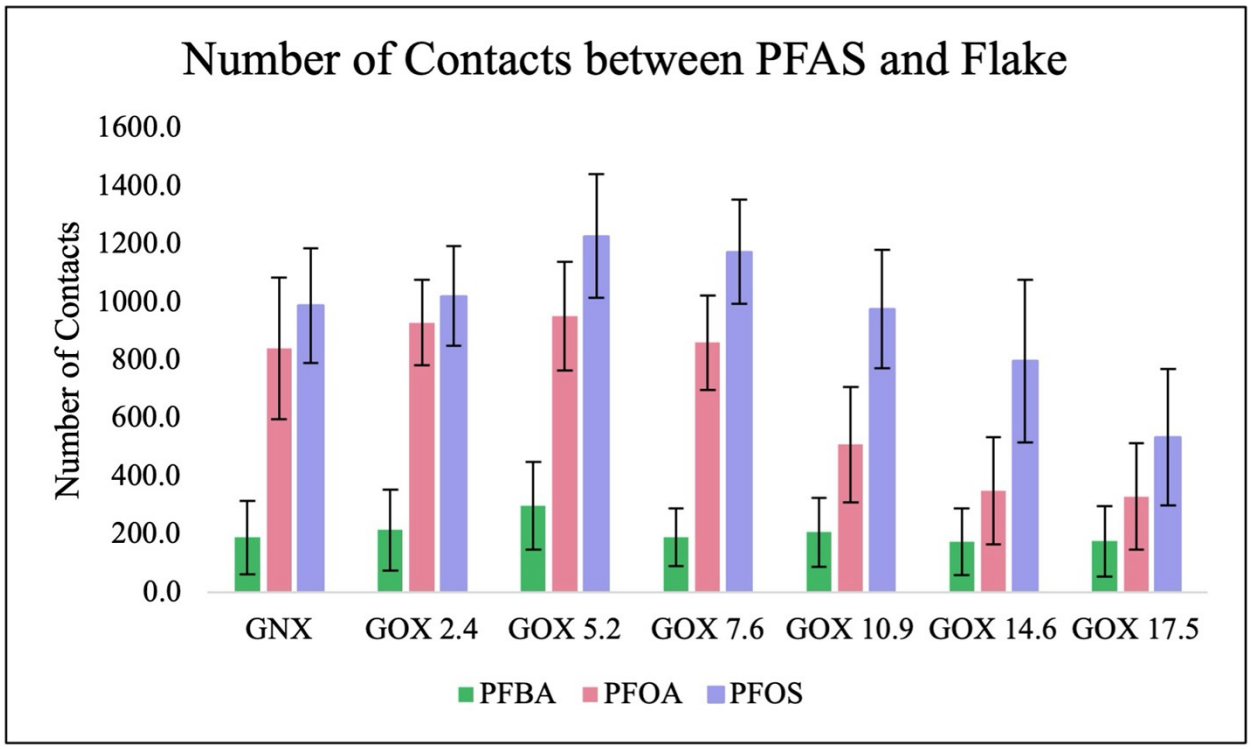

Figure S3: Number of Contacts between PFAS and Flakes. The number of contacts is the sum of the native and nonnative contacts. The cutoff distance was set at 5 Å.

S7: Linear Interaction Energy of Species with Water

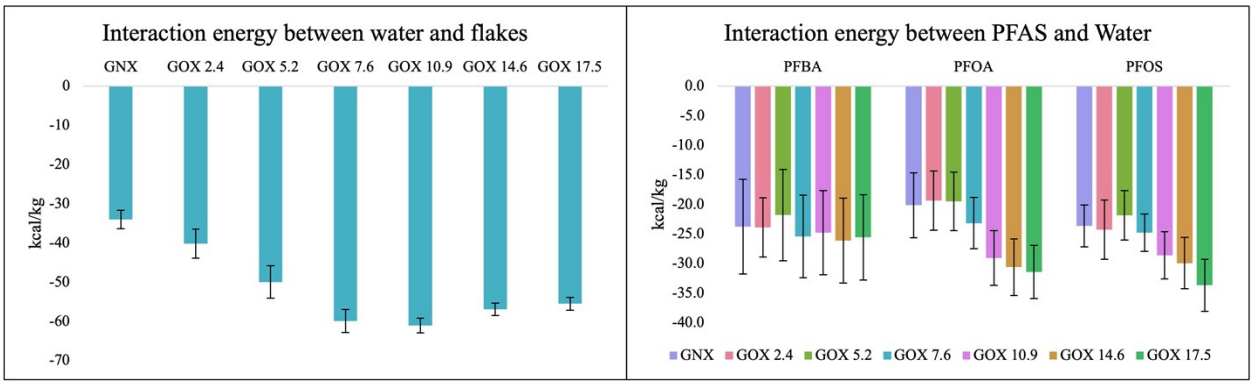

Figure S4: Left panel – LIE of water interaction with flakes normalized by mass of flake. Right panel – LIE of PFAS interaction with water normalized by mass of PFAS

The left panel of Figure S4 shows the LIE of water with PFAS normalized by mass of the flake. The interaction between water and the flake is the strongest for GOX 7.6 and GOX 10.9. The interaction energy then decreases slightly for GOX 14.6 and GOX 17.5. This suggests that the oxidation level of GOX 7.6 and GOX 10.9 maximizes water interactions by cluster formation. The slight decrease and plateau at GOX 14.6 and GOX 17.5 indicates that the surface area available via cluster formation has been maxed out.

The right panel of Figure S4 shows the PFAS interaction with water normalized by the mass of the PFAS. Water interaction with PFBA is similar in the presence of all flakes, indicating that the PFBA interacts mostly with water. Meanwhile, PFOA and PFOS have a lower interaction energy with water in the presence of low oxygen coverage flakes. The water interaction with PFAS increases as the oxidation increases after GOX 7.6. As the oxygen coverage of the flake increases, PFAS interact more with the water.

S8: Radial Distribution Functions Calculated

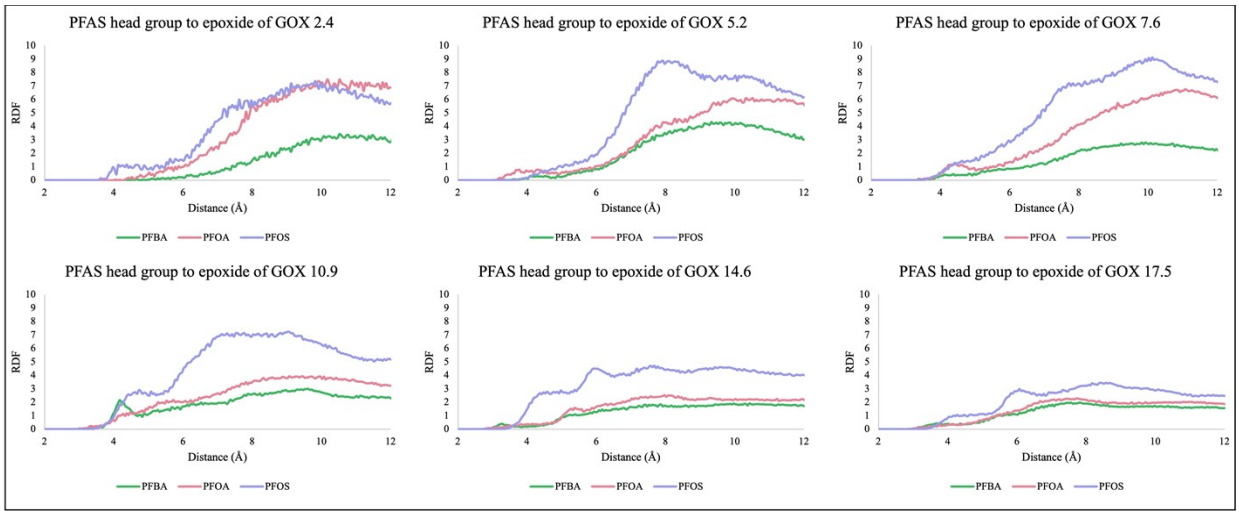

Figure S5: RDFs of PFAS head group to epoxide of flake

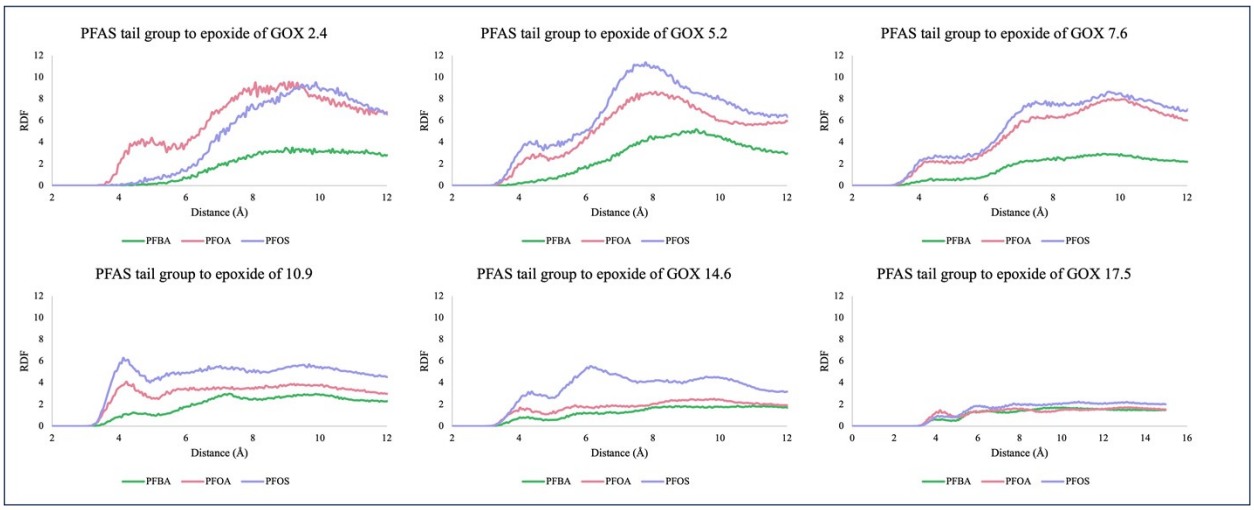

Figure S6: RDFs of PFAS tail group to epoxide of flake

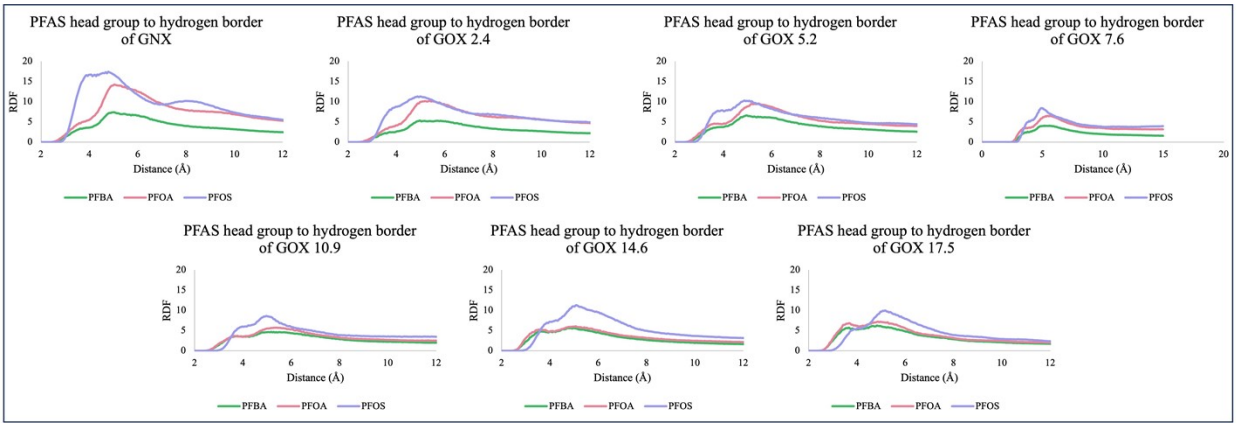

Figure S7: RDFs of PFAS tail group to hydrogen border of flake