Oxidized and Si-doped Graphene: Emerging Adsorbents for Removal of 1,4-Dioxane

Diego Cortés-Arriagada[*,1], *Sebastián Miranda-Rojas*[2], *Daniela E. Ortega*[3], *and Alejandro Toro-Labbé*[3]

[1]Programa Institucional de Fomento a la Investigación, Desarrollo e Innovación. Universidad Tecnológica Metropolitana. Ignacio Valdivieso 2409, P.O. Box 8940577, San Joaquín, Santiago, Chile. *E-mail address: dcortes@utem.cl

[2]Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andrés Bello, Avenida República 275, Santiago, Chile.

[3]Laboratorio de Química Teórica Computacional (QTC), Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Macul, Santiago 9900087, Chile.

Supporting Information

S1. Energy decomposition analyses of the G- and GO-dioxane systems.

S2. Partial density-of-states plots of systems 10a-10b.

S3. Adsorption of 1,2-dioxane and 1,3-dioxane onto GO and SiG.

S4. Adsorption of 1,4-dioxane onto N- and S-doped graphene.

S1. Energy decomposition analyses of the G- and GO-dioxane systems.

Table S1. Energy decomposition analysis of the adsorption energy in the pristine and GO systems ($-E_{ads}=\mathit{\Delta} E_{prep}+\mathit{\Delta} E_{int}$). Energies are in eV.[a] Adsorption energies were calculated with the ADF package. E_{vdW2} is the recalculated dispersion contribution using ADF.

system	$E_{ads}{}^{a}$	ΔE_{prep}	ΔE_{oi}	ΔE_{elst}	ΔE_{Pauli}	E_{vdW2}
withpristinegraphene						
1:G–dioxane	0.33	0.00	-0.11	-0.27	0.49	0.44
withoxydizedgraphene						
2: GO$^{\text{hydroxyl}}$–diox	0.56	0.03	-0.44	-0.78	1.07	0.44
3: GO$^{\text{epoxide}}$–diox	0.37	0.00	-0.13	-0.36	0.54	0.43
4: GO$^{\text{carboxyl}}$–diox	0.43	0.06	-0.59	-0.83	1.02	0.09
5: GO$^{\text{carbonyl}}$–diox	0.26	0.01	-0.15	-0.29	0.45	0.28
6a: GO$^{\text{multi-hydroxyl}}$–diox$_{a}$	0.81	0.10	-0.96	-1.30	1.77	0.43
7a: GO$^{\text{multi-epoxide}}$–diox$_{a}$	0.42	0.00	-0.23	0.60	0.87	0.46
8a: GO$^{\text{multi-carboxyl}}$–diox$_{a}$	0.56	0.06	-0.67	-0.99	1.22	0.18
9a: GO$^{\text{multi-carbonyl}}$–diox$_{a}$	0.26	0.00	-0.12	-0.26	0.40	0.28

From this analysis, it is possible to infer that the electronic part of the interaction between the carboxyl in the monosubstituted GO and dioxane is stronger than the substituted with a hydroxyl group, in opposition to the final adsorption energies. This is expected as the proton from the carboxyl is more electronic deficient than the one from the hydroxyl group, allowing to it to develop a larger orbital overlap with the lone-pair from the oxygen of dioxane. Therefore, the nature of the hydrogen bond (HB) formed between the dioxane and the carboxyl group involves a higher covalent character compared with the interaction with a hydroxyl group. However, as the carboxyl group is located at the edge of the surface, it lacks the dispersive contribution coming from the contact between the dioxane and graphene surface, interaction that is present in the system with hydroxyl and determines its higher adsorption energy. This remarks the relevance of the dispersion interactions in the adsorption process and how it determines the final strength of the interaction. Another feature of the systems is revealed after the analysis of their multisubstituted counterparts, where the system with hydroxyl groups presents a higher orbital contribution than the one with carboxyl groups, even despite the fact that in this multisubstituted system, the dioxane only interacts with one hydroxyl group. The main reason for this increase in the orbital contribution is due to the inner HB network formed between the hydroxyl groups from the GO, which increase the acidity of the hydroxyl proton by stabilizing the charge in the donor oxygen. This is evidenced after the analysis of the interaction distances, which decreased from 1.74 to 1.54 Å from single- to multisubstituted GO, while the O-H bond distance in the hydroxyl group is increased from 1.00 to 1.03 Å from single- to multisubstituted GO, denoting the weakening of the O-H bond. As exposed by the AIM analysis, the systems substituted with epoxide and carbonyl groups showed an electronic interaction of repulsive nature, only stabilized by the dispersion interactions. To understand the origin of this repulsive character, we first have to define the steric repulsion term, which is the sum of ΔE_{elst} and ΔE_{Pauli} as follows:

$$\Delta E_{steric} = \Delta E_{elst} + \Delta E_{Pauli}$$

This steric term corresponds to the commonly used concept of steric interaction or electronic repulsion. If we compare the steric term from the multisubstituted hydroxyl GO with the orbital term, we obtain that the latter is 0.47 eV more stable, thus revealing the stabilizing character of the covalent contribution to this interaction. Meanwhile, for the systems substituted with epoxide and carbonyl groups, the comparison between the steric and orbital terms always lead to an outcome, where the orbital stabilization is not enough to compensate the steric repulsion, therefore resulting in a repulsive interaction from the electronic point of view. Thus, these complexes are only stabilized by the dispersion forces.

S2. Partial density-of-states plots of systems 10a–10b.

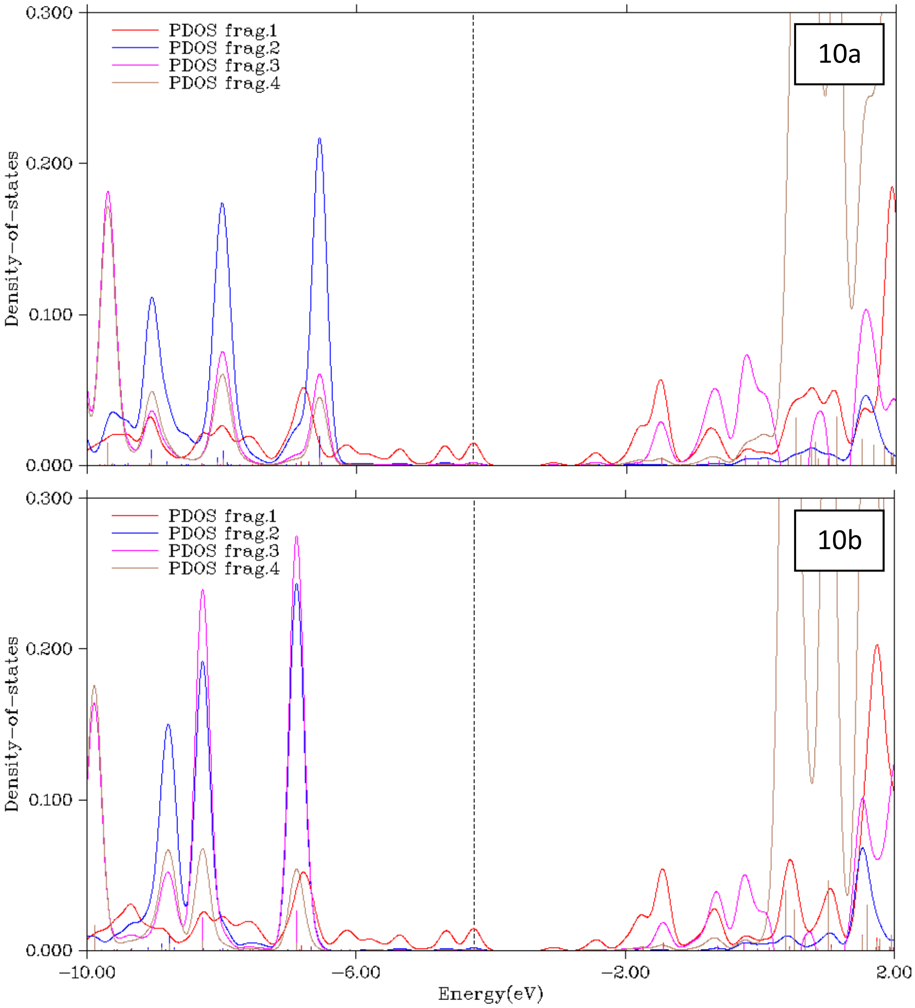
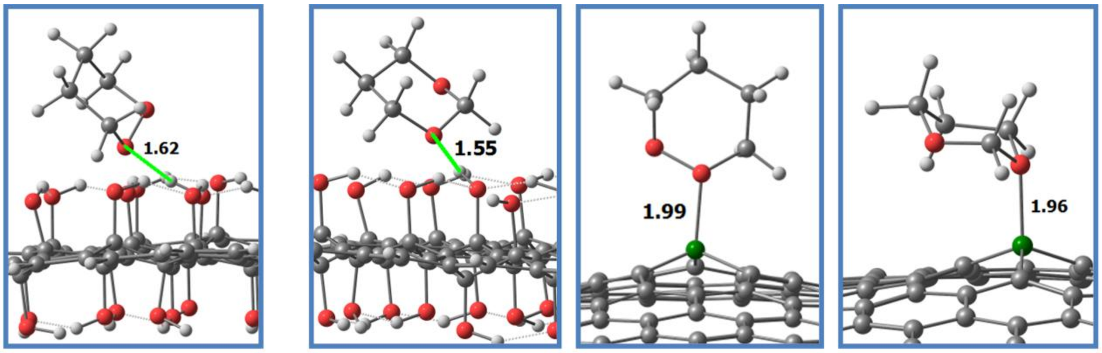


Fig. S1 Partial density-of-states of SiG-dioxane systems **10a–10b**. The dotted line indicates the HOMO level; frag. 1 contains the Si atom of SiG; frag. 2 contains the oxygen atoms of 1,4-dioxane; frag. 3 contains the carbon atoms of 1,4-dioxane; frag. 4 contains the hydrogen atoms of 1,4-dioxane. Orbital energies are not scaled in the DOS plots.

S3. Adsorption of 1,2-dioxane and 1,3-dioxane onto GO and SiG.



$GO^{multi\text{-}hydroxyl}\cdots$1,2–dioxane E_{ads}= 0.71 eV

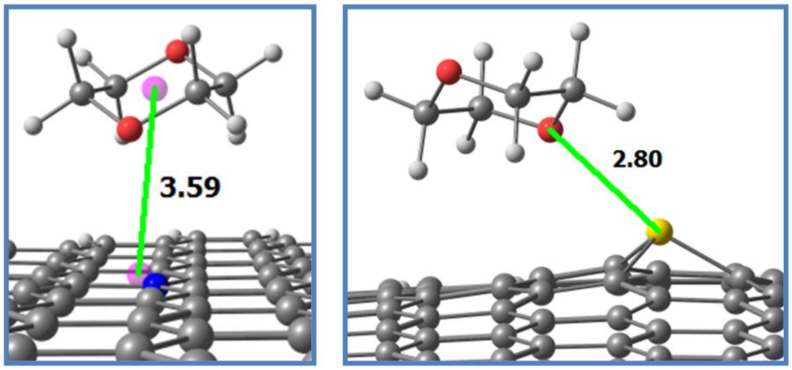
$GO^{multi\text{-}hydroxyl}\cdots$1,3–dioxane E_{ads}= 0.70 eV

SiG···1,2–dioxane E_{ads}= 0.55 eV

SiG···1,3–dioxane E_{ads}= 0.75 eV

Fig. S2 Most stable adsorption configurations and adsorption energies (E_{ads}) of 1,2-dioxane and 1,3-dioxane onto GO and SiG. Distances are in angstroms (Å). Color code: White (H), grey (C), red (O), green (Si). The multi-functionalized GO system with hydroxyls was considered as a model of GO.

S4. Adsorption of 1,4-dioxane onto N- and S-doped graphene.



NG···1,4–dioxane
E_{ads}= 0.39 eV

SG···1,4–dioxane
E_{ads}= 0.40 eV

Fig. S3 Most stable adsorption configurations and adsorption energies (E_{ads}) of 1,4-dioxane onto nitrogen doped graphene (NG) and sulfur doped graphene (SG). Distances are in angstroms (Å). Color code: White (H), grey (C), blue (N), red (O), green (Si), yellow (S).