Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

Adsorption of sodium diclofenac on graphene: a combined experimental and theoretical study

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S1. Structural and electronic properties of sodium diclofenac

Optimized structure, electronic levels and local density of charges to Sodium DCF (s-DCF) are show in Figure S1. Thus s-DCF molecule does not present a planar geometric configuration throughout your entire length i.e., benzene rings are located on different planes, exhibiting a torsional angle between the two rings, which may be unfavorable to π-π interactions between this molecule and the planar graphene.

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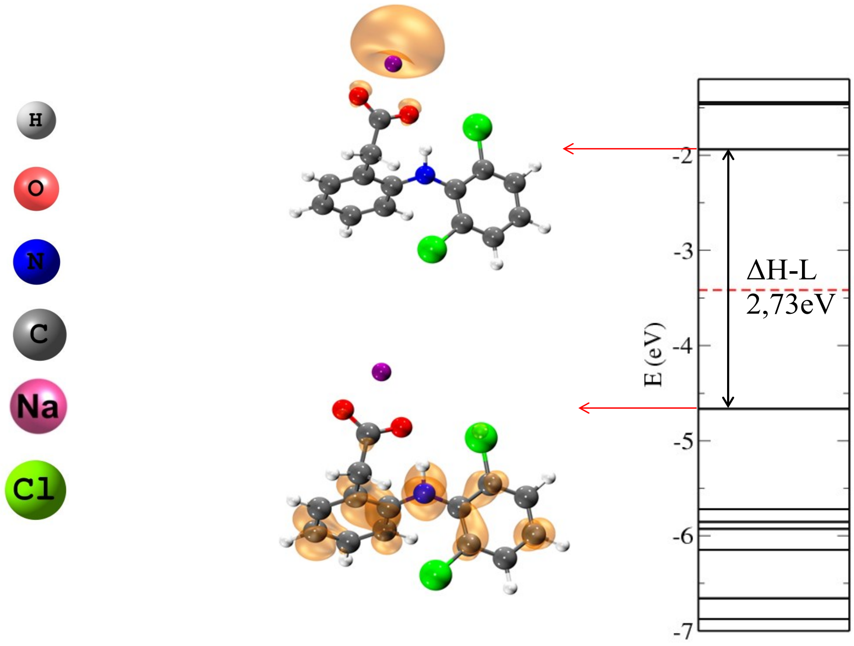

Fig. S1. Optimized structure, electronic levels and local density of charges to s-DCF.

From energy levels, the HOMO-LUMO difference (ΔH-L) stay around 2.73eV, which guarantee greater "stability" (low reactivity) to diclofenac. This difference can be further correlated with hardness and softness chemical concepts. Both concepts are well defined by DFT where the softness are linearly related to polarizabilities of atoms; i.e. their ability to accept or donate charges [1-2]. Further, other authors evaluated that hardness measures the resistance imposed by a molecule to a change in its electronic distribution, being a good measure of aromaticity [3]. From charge density of s-DCF, one can observe that for HOMO the density is located primarily on the aromatic rings, thus indicating a concentration of free electrons on these rings, revealing a great capacity of these rings to donate charges. As for the LUMO, the charge density is concentrated on Na+ ion, as this atom is protonated.

S2. Structural and electronic properties of graphene and their oxides

The optimized molecular structure of graphene reveals a planar geometric configuration throughout its entire length, being C-C distance around 1.42Å (Fig. S2 (A)). The conduction and valence bands meet at the K point of the Brillouin zone. All these results are in complete accordance with findings on literature [4-5].

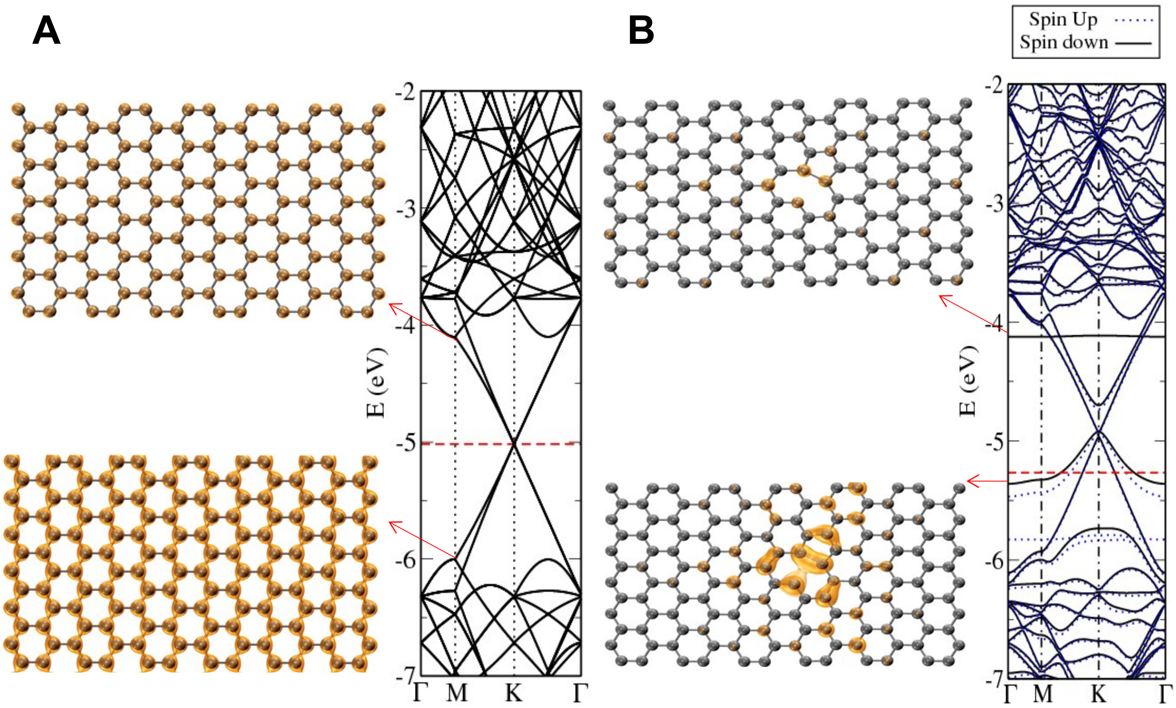

Fig. S2. Optimized structure, density of charges and band structure to (A) pristine graphene, (B) graphene plus a vacancy.

Creating a vacancy on graphene by removing a C atom, leads to a distortion on the surface of graphene and repositioning of atoms, originating a pentagon on hexagonal structure of graphene plane. Thus, the bond distance between two neighboring atoms in pentagon varies to 1.76Å. In addition, there is a small displacement (~0.1Å) out of the basal plane of graphene, from the atom on the opposite side of former pentagon (Fig. S2 (B)). All these distortions takes a hybridization levels and a spin polarization about 1.16 μB in graphene. These results were also observed by Yuchen and coworkers [6].

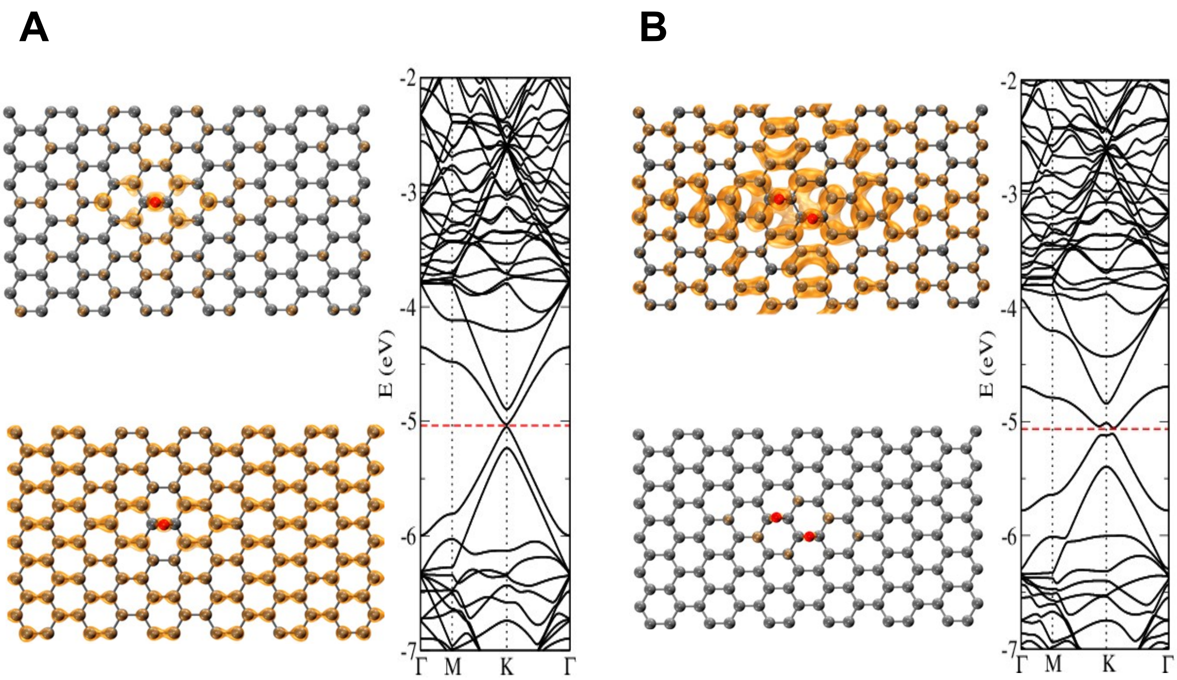

Fig. S3. Optimized structure, density of charges and band structure to (A) graphene + 1 epoxy group, (B) graphene + 2 epoxy groups.

For epoxy functionalized graphene, the functional groups exhibit a displacement out of graphene plane, being more significant to graphene with two epoxy groups (about 0,45Å). The C-O distance, was around 1.44Å while the C-C distance, near functional groups, increased to 1.51Å for one other two epoxy groups (Fig. S3 (A),(B)). Similar results were founded on literature [7]. Breaking on symmetry, degeneration levels and also a gap opening on graphene (more visible to graphene with 2 epoxy), also was verified, and is complete accordance with other results [7-8].

To graphene functionalized with one or two hydroxyl groups, once again where found a displacement of carbon atoms out of basal graphene plane around 0.44Å to one hydroxyl group, and 0.53Å for two hydroxyl groups. The C-C distance on hydroxyl groups was approximately 1.51Å, while C-O and O-H distances stay around 1.48Å and 0.98Å respectively (Fig. S4 (A),(B)). All these results are in accordance with the literature [7]. The atomic distortions of graphene plane lead to a separation of some degenerate levels. The presence on band structure of a flat level between the valence and conduction band, as well as a opening of a small gap (~ 0,1eV) are also noticed, and already have been reported by Jia-Yan An and MY Chou [7]. Degenerate levels and a gap opening (~0.2 eV) become even more evident to graphene functionalized with two hydroxyl groups, in accordance with literature [7].

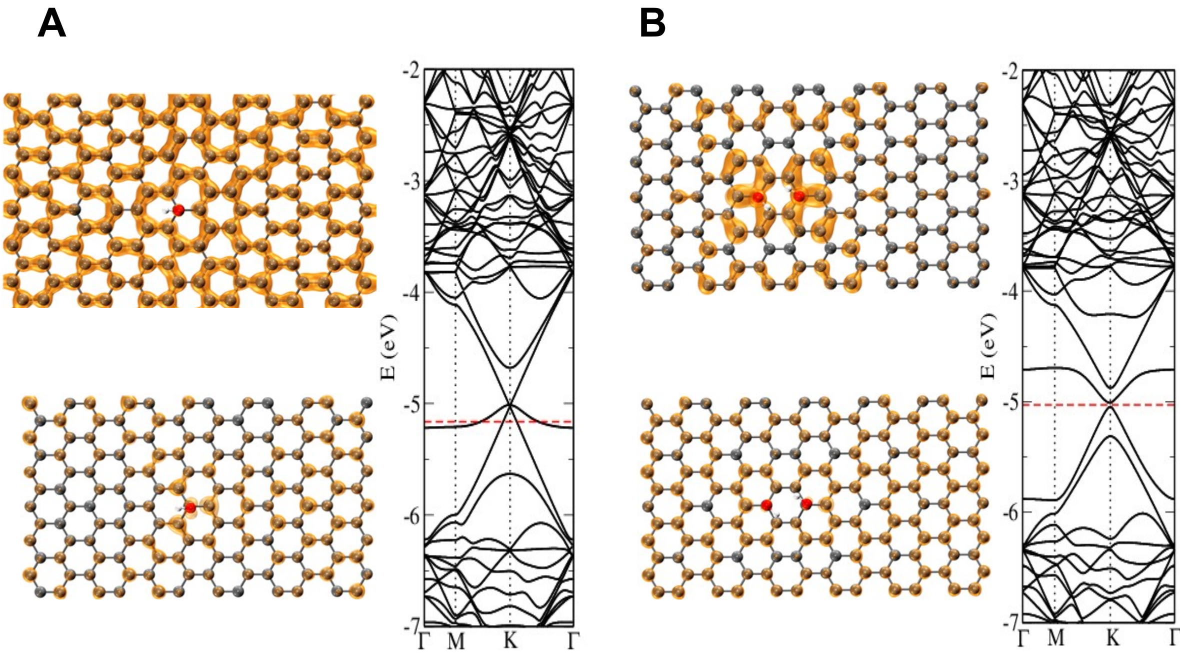

Fig. S4. Optimized structure, density of charges and band structure to (A) graphene + 1 hidroxyl group, (B) graphene + 2 hydroxyl groups.

Regarding as graphene nanoribbons functionalized with one or two carboxyl groups respectively (Fig. S5 (A),(B)), it was founded that carbon atoms of hydroxyl groups present a displacement out of nanoribbon plane around 1.35Å and 1.44Å to one and two functional groups, respectively. Furthermore, to one carboxyl group the angle between O_1-O_2 was 121.88°, while the angle O_2-H was 103.94°. The distances between C-C, O_1-O_2 and O_2-H, were around 1.22Å; 1.35Å and 0.99Å, respectively. For two carboxyl groups the angle between O_1-O_2 was 120.9°, while the O_2-H angle was 105°. The distances between C-C; O_2-O_1 and O_2-H, were similar to the previous ones, i.e. around 1.22Å; 1.35Å and 0.99Å, respectively (Fig. S5 (A),(B)). This results are consistent with other found by Sodi and coorkers [9].

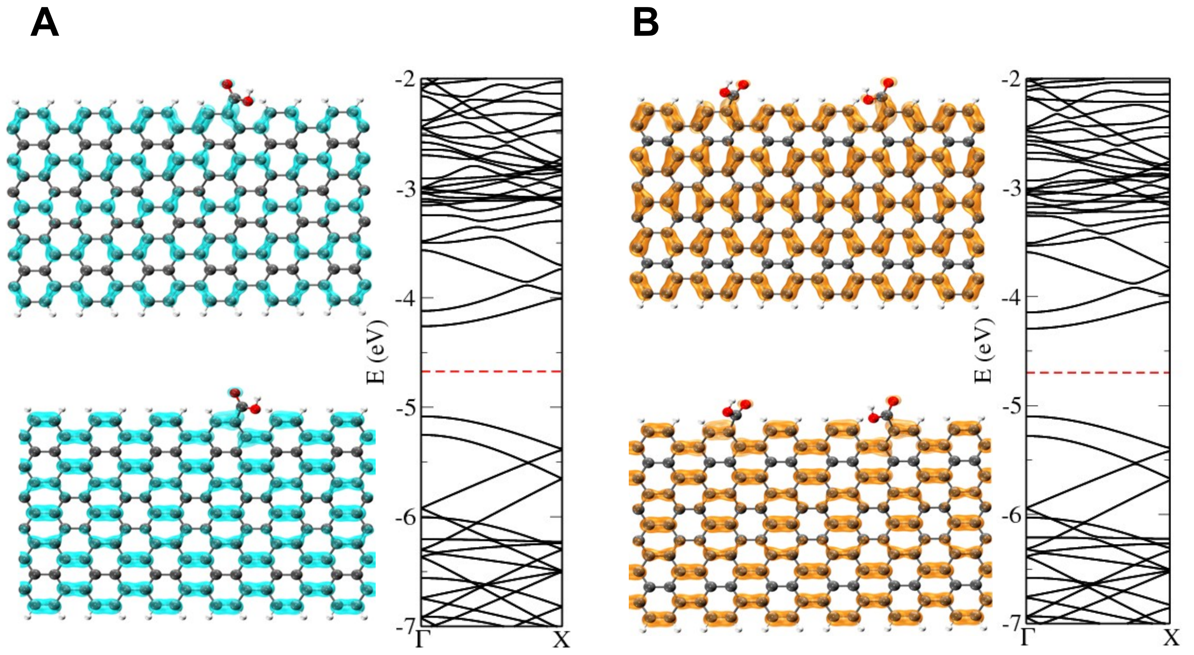

Fig. S5. Optimized structure, density of charges and band structure to (a) graphene nanoribbon + 1 carboxyl group, (b) graphene nanoribbon + 2 carboxyl groups.

To configurations evolving grapehene nanoribbons functionalized with one or two carbonyl groups, respectively (Fig. S6 (A),(B)), it was founded that functional groups remained at the same height in relation to nanoribbon plane, unlike to carboxyl group. Furthermore, for both, nanorribon with one or two carbonyl groups, C-O distances were approximately 1.25Å, whereas the distances between neighboring carbon of carboxyl group are in the range of 1.43Å to 1.47Å. Also can be notice the presence of flat levels on the Fermi level (Fig. S6 (A),(B)). This can be attribute to C-O functional group, where in these cases shows absence of 1 electron. Thus, there is a strong trend of this functional group to receiving one electron.

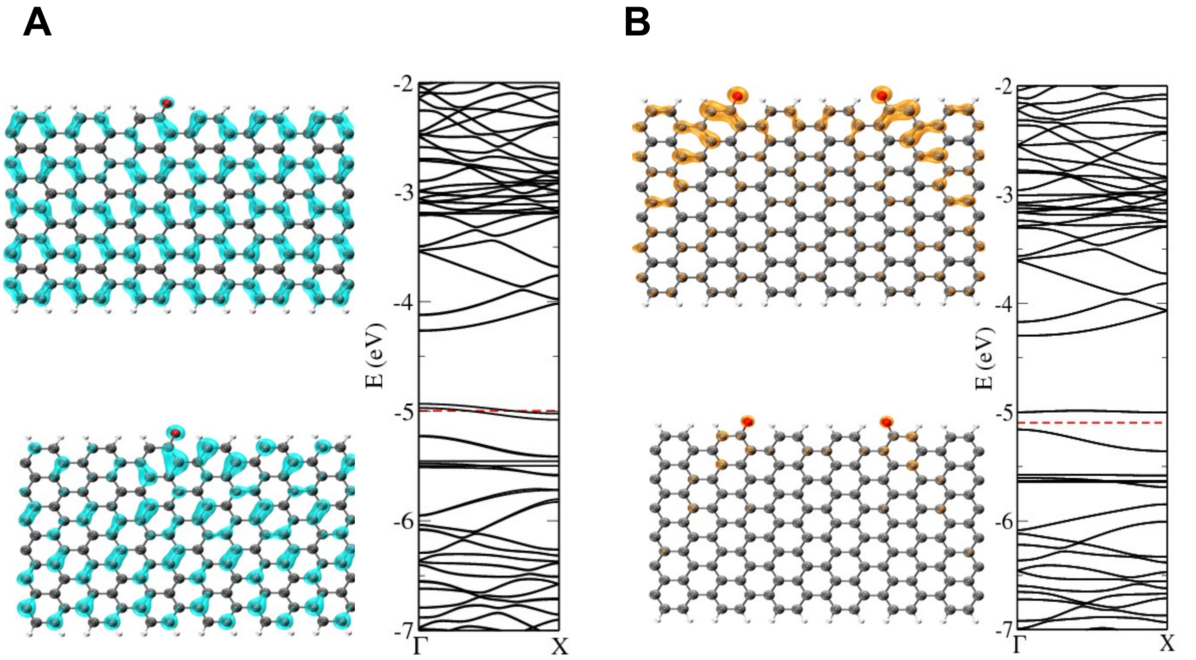

Fig. S6. Optimized structure, density of charges and band structure to (a) graphene nanoribbon + 1 carbonyl group, (b) graphene nanoribbon + 2 carbonyl groups.

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