Letter to the editor

Switchable hydrophobicity/hydrophilicity of a HOPG surface - Comment on the paper by Y. Wei and C.Q. Jia, Carbon, 87 (2015) 10-17

A B S T R A C T

Based on simulation data we show that the edge graphite atoms of a HOPG surface have remarkable influence on water contact angle values. Compared to graphite basal plane, a water droplet sitting on the edge atoms experiences two effects on wettability, smaller density of surface carbon atoms and the appearance of the Wenzel states. The differences between contact angles recorded for samples containing different amounts of the edge atoms are large, even after carbon surface oxidation. Thus, we report anisotropic wettability of the graphite surface. Moreover, changing the content of edge atoms in the substrate, one can induce switchable hydrophilic/hydrophobic properties of graphite.

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Recently Wei and Jia [1] reported (for the first time) very interesting results of water contact angle (WCA) measurements on the edge surface of highly oriented pyrolytic graphite (HOPG). To do this the HOPG samples purchased from Mikro Masch (Grade: ZYH) were applied. Freshly prepared surfaces were obtained by the application of Scotch tape method, next polished by a sandpaper and polished again using acid-free multi-purpose paper. Next the edge surfaces having different angles to the basal surface (−30°, −60° and −90°; the samples labeled as HOPG-Side-30°, HOPG-Side-60° and HOPG-Side-90°, respectively) were prepared. For all samples the WCA was measured (using Goniometer at open air condition and the relative humidity of 40–50%) to check how it depends on time and, what is more important for our study, how it depends on the type of carbon atoms present on the substrate surface. The authors reported the WCA values for the basal plane HOPG as equal to 61.8 ± 3.3°. After 2h air exposure it increased to 76.3 ± 2.4°. After 1d (air exposure) the stabilization of the WCA was observed at 81.9 ± 2.9°. The authors have not recorded the statistically important differences between the WCA values measured for HOPG-Side-30°, HOPG-Side-60° and HOPG-Side-90° (the reported values were equal to 62.0 ± 8.7°, 60.9 ± 9.2° and 56.2 ± 8.4°, respectively). The average WCA (60.8 ± 9.0°) for the three samples was close to this reported for the basal plane HOPG sample. Moreover, this WCA, in contrast to that observed for the basal plane HOPG, was time independent.

Molecular simulations can be used to gain deeper insights into experimental results (see for example [2]), and this is the major subject of our comment. By means of a molecular dynamics (MD) method the droplets containing 2000 TIP4P/2005 [3] water molecules were simulated (using the OPENMM toolkit for MD simulation supported by Python 3.4.5. [4]) to check the influence of graphite edge surface atoms on the WCA. The details of the simulation technique are provided in Supplementary Data. One should note that the value of carbon-oxygen potential well depth is chosen in such a way that the effect of the line tension on the simulated WCA is very small [see Supplementary Data].

Fig. 1 shows that simulated WCA for the basal-plane HOPG model is (in the range of experimental error) the same as observed during the experiment reported in Ref. [1]. There are practically no differences between the arm-chair and zig-zag structures, excepting the HOPG-Side-90°, where a slightly smaller angle is recorded for the zig-zag structure. One can see that the values of WCA progressively increase with the rise in the side angle. Thus, the basal-plane HOPG surface is hydrophilic, while the remaining surfaces are hydrophobic. One can see that in this way the HOPG surface manifests its anisotropic properties. To explain the observed differences, the potential energy of water interaction with all surfaces was calculated.

The results collected in Fig. 2 show, that if one takes into account only the contribution of the potential energy of water-HOPG interactions on the solid-liquid surface tension, the differences between WCA for HOPG-Side-30° and HOPG-Side-60° should be negligible. Moreover, both surfaces should provide the largest WCA values. At the same time, WCA values should be the smallest for the basal plane HOPG followed by the HOPG-Side-90°. However, Fig. 1 shows that the angles for HOPG-Side-30° and HOPG-Side-60° are not the same, moreover they are not remarkably larger than that calculated for HOPG-Side-90°. Therefore, it was hypothesized that the effect substantially decreasing the WCA would affect both structures. To check this hypothesis the density profiles of water in the vicinity of substrate surfaces were calculated (with selected results compared in Fig. 3). These profiles were obtained
by the projection of a 1 nm internal slab of the droplet on the \(xz\) plane. One can see, that for HOPG-Side-30° and HOPG-Side-60° as well as for HOPG-Side-90° (to smaller degree), the Wenzel effect [5] is observed. This effect increases substrate surface wettability leading to a decrease in the WCA values.

The authors of [1] explained the similarity between the WCA for basal-plane HOPG and the average WCA measured for HOPG-Side-30°, HOPG-Side-60° and HOPG-Side-90° as a result of the presence of surface oxygen groups (oxidation theory). In fact it is well known that the occurrence of oxygen on different surfaces can lead to the decrease in the WCA value [6–8]. This is why at the next stage, we prepared the oxidised HOPG surface models. The type and the mechanisms of creation of surface oxygen groups attached to the edge HOPG carbon atoms is still the subject of debate [9,10]. However, Wei and Jia [1] reported the XPS spectra of surface groups present on multi-grain graphite. Based on their results, oxidised HOPG surfaces were prepared. It was assumed that the oxygen is present in the amount of 6.5% of surface atoms, and the ratio of groups was calculated based on the tabulated XPS data in Ref. [1]. In this way the models of HOPG(ox)-Side-30°, HOPG(ox)-Side-60° and HOPG(ox)-Side-90° surfaces were obtained. Fig. 4 shows the snapshot of HOPG(ox)-Side-90°, and Fig. 5 shows the results of the simulated WCA for zig-zag structures.

The results in Fig. 5 when compared to those of Fig. 1, show that the oxidation of HOPG surfaces decreases the WCA values. This is caused by the rise in the solid surface tension. However, simulation data show that the WCA are not the same, contrary to the experimental results collected in Ref. [1]. Additionally, the Wenzel effect is still observed, even after surface oxidation (see Fig. 3).

Summing up, based on the MD simulation data we show that the presence of the edge graphite atoms should lead to significant changes in the WCA values. These differences are caused by smaller (compared to the basal plane graphite) density of surface carbon atoms (leading to the rise in WCA values [11]). Moreover Wenzel states appear and they decrease the values of the WCA. The differences between WCA recorded for different samples are still present even after carbon surface oxidation. We also report the anisotropic wettability of the HOPG surface. Thus, by changing the content of edge atoms in the substrate one can observe switchable hydrophilic/hydrophobic properties, since the WCA changes across the range of 64.3° (for basal plane HOPG) - 103.4° (for HOPG-Side-90°).

Considering the results of our study alongside the results presented by Wei and Jia [1], one can conclude that the preparation...
of an HOPG surface composed of the edge atoms is still a difficult challenge.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2017.01.048.

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Fig. 4. Snapshot showing random distribution of oxygen groups on the HOPG(ox)-Side-90° surface (created using the VMD software [12]). (A colour version of this figure can be viewed online.)

Fig. 5. The influence of HOPG surface oxidation on the WCA values for zig-zag surfaces. (A colour version of this figure can be viewed online.)