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Modeling of Graphite Oxide

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Abstract: Based on density functional calculations, optimized structures of graphite oxide are found for various coverages by oxygen and hydroxyl groups, as well as their ratio corresponding to the minimum of total energy. The model proposed describes well-known experimental results. In particular, it explains why it is so difficult to reduce the graphite oxide up to pure graphene. Evolution of the electronic structure of graphite oxide with the coverage change is investigated.

1. Introduction

Despite the fact that graphite oxide (GO) was first derived more than a century ago^{1,2} its structure and chemical composition remains unclear. GO can be used for production of graphite nanoparticles and an insulating material for nanodevices.^{3,4} Recently, after discovery of extraordinary electronic properties of single-layer carbon, graphene,^{5–8} and successful exfoliation of layers in GO^{9,10} it is considered as a perspective source of a “cheap graphene”.³ Direct structural information about GO can hardly be obtained (for most structural methods, the use of bulk crystals are desirable whereas the GO exists mainly in solutions) which makes theoretical modeling of its structure and properties especially important.

Original methods of preparation of GO have been modified^{11–14} which allows slight variation of its chemical composition. In a report by Nakajima and Matsuo¹¹ the chemical compositions of GO derived by the methods developed by Brodie¹ and Staudenmaier² were determined as $C_8H_{2.54}O_{3.91}$ and $C_8H_{4.61}O_{6.70}$, respectively. This means that both hydroxyl groups connected with single carbon atoms and oxygen atoms connected with two carbon atoms present in GO (see Figure 1). According to Szabó and co-workers,¹² the chemical composition

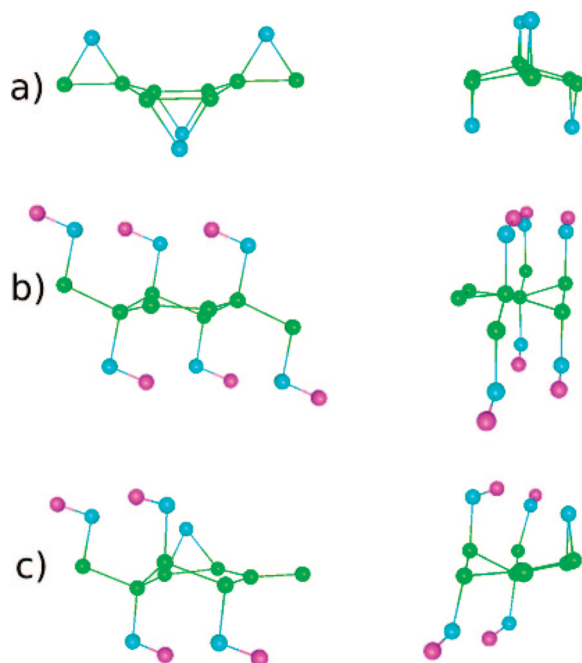


Figure 1. The most stable configurations of graphene functionalized by oxygen only (a), hydroxyl groups only (b), and both oxygen and hydroxyl groups (c). Carbon, oxygen, and hydrogen atoms are shown in green, blue, and violet, respectively.

of different samples of GO varies from $C_8H_{1.20}O_{3.12}$ to $C_8H_{1.60}O_{3.92}$, according to Hontora-Lucas et al.¹³ from $C_8(OH)_{1.38}O_{0.63}$ to $C_8(OH)_{1.64}O_{0.79}$, and according to Cassagneau and co-workers¹⁵ from $C_{12}HO_2$ to $C_{15}H_3O_4$. In general, one can conclude that the chemical composition of GO, not considering groups coupled with graphene edges, varies in a range from $C_8H_2O_3$ to $C_8H_4O_5$. It is a common opinion (see the papers cited above) that oxygen in GO is mainly present in hydroxyl groups or in bridges connecting two carbon atoms in graphene layers whereas the amount of carboxyl, as well as carbonyl, groups is relatively small. Thus, the two limiting compositions of GO can be presented as $C_8(OH)_2$ and $C_8(OH)_4O$. All chemical

(15) Cassagneau, T.; Guérin, F.; and Fendler, J. *Langmuir* **2000**, *16*, 7318.

- (1) Brodie, B. C. *Ann. Chim. Phys.* **1860**, *59*, 466.
- (2) Staudenmaier, L. *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 1481.
- (3) Ruoff, R. *Nature Nanotechnol.* **2008**, *3*, 10.
- (4) Hirata, M.; Gotou, T.; Horiuchi, S.; Fujiwara, M.; Phiba, M. *Carbon* **2005**, *43*, 503.
- (5) Geim, A. K.; and Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 183.
- (6) Katsnelson, M. I. *Mater. Today* **2007**, *10*, 20.
- (7) Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. *Rev. Mod. Phys.* **2008**, *80*, 315.
- (8) Katsnelson, M. I.; Novoselov, K. S. *Solid State Commun.* **2007**, *143*, 3.
- (9) Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature (London)* **2006**, *442*, 282.
- (10) Dikin, D. A.; Stankovich, S.; Zimney, E. J.; Piner, R. D.; Dommett, G. H. B.; Eremenko, G.; Nguyen, S. T.; and Ruoff, R. S. *Nature (London)* **2007**, *448*, 457.
- (11) Nakajima, T.; and Matsuo, Y. *Carbon* **1988**, *26*, 357.
- (12) Szabó, T.; Tombácz, E.; Ille's, E.; Dékány, I. *Carbon* **2006**, *44*, 537.
- (13) Hontora-Lucas, C.; López-Peñado, A. J.; de D. López-González, J.; Rojas-Cervantes, M. L.; Martín-Aranda, R. M. *Carbon* **1995**, *33*, 1585.
- (14) Stankovich, S.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Carbon* **2006**, *44*, 3342.

formulas of GO obtained experimentally manifest the coverage of graphene between 25% and 75%, which means that, at least, a quarter of the carbon–carbon bonds in the graphene layer are double bonds whereas the rest are single bonds like in a diamond. Indeed, both XPS^{13,16} and infrared¹⁷ spectroscopy data confirm coexistence of sp^3 and sp^2 electron configurations of carbon.

Based on experimental data¹¹ and additional measurement results, a model of GO has been suggested by Nakajima and co-workers.¹⁸ According to this model, the GO structure is intermediate between two ideal structures, C_8O_2 and $C_8(OH)_4$ (Figure 2c and 2h, respectively). Later models^{19,20} differ mainly by assumptions concerning edge groups. As a result, the GO structure is described as a combination of completely covered and completely uncovered stripes of graphene which is confirmed also by recent theoretical results.^{21,22} Recently, mechanical properties of GO have been simulated, based on modeling of nanoobjects functionalized by oxygen from one side²³ or on experimental data on chemical composition of GO.²⁴

However, due to the stripes of uncovered graphene, GO should be conducting, according to these models. At the same time, experimentally GO becomes conducting only after a very strong reduction^{4,25} whereas typically GO is insulating. Here, based on density functional calculations, we formulate a model of insulating GO. We also investigate a transition to conducting state at the reduction and explain why it is so difficult to clean GO completely and to derive pure graphene from GO.

2. Computational Methods

Some general factors determining chemical functionalization of graphene have been investigated in our previous work²⁶ using hydrogenization as an example. First, graphene is a very flexible material, a chemisorption of even a single hydrogen atom leads to essential distortions of the graphene sheet with a radius approximately 5 Å, and these lattice distortions are of crucial importance for energetics of the process. Second, for the chemisorption of two hydrogen atoms, the configuration where they are bonded with two neighboring carbon atoms from opposite sides of the sheet turns out to be the most energetically favorable. Third, complete coverage by hydrogen provides the global minimum of energy. These features are relevant, as we will show here, also for the case of GO.

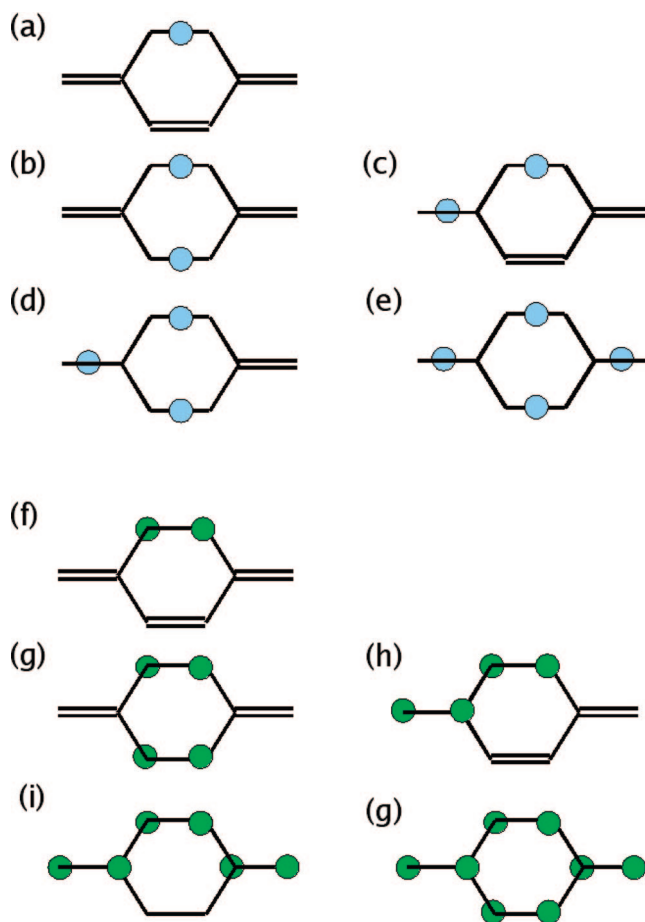


Figure 2. A sketch of functionalization of graphene by (a–e) oxygens (blue circles), and (f, g) hydroxy groups (green circles).

We used the pseudopotential density functional SIESTA package for electronic structure calculations^{27,28} with the generalized gradient approximation for the density functional,²⁹ with energy mesh cutoff 400 Ry, and k -point $11 \times 11 \times 1$ mesh in the Monkhorst–Park scheme.³⁰ During the optimization, the electronic ground states were found self-consistently by using norm-conserving pseudopotentials to cores and a double- ζ plus polarization basis of localized orbitals for carbon and oxygen, and double- ζ one for hydrogen. Optimization of the bond lengths and total energies was performed with an accuracy 0.04 eV/Å and 1 meV, respectively. This method is frequently used for computations of the electronic structure of graphene.^{26,31–33}

To compute the properties of layered GO we have carried out calculations of the corresponding structures for the case of 25% coverage by hydroxyl groups. Instead of GGA, we use here the LDA approximation which is known to be more accurate to describe interlayer coupling in graphite and other van der Waals systems.³⁴

- (16) Jeong, H.-K.; Lee, Y. P.; Lahaye, R. J. W. E.; Park, M.-H.; An, K. H.; Kim, I. J.; Yang, C.-W.; Park, C. Y.; Ruoff, R. S.; and Lee, Y. H. *J. Am. Chem. Soc.* **2008**, *130*, 1362.
- (17) Fuente, E.; Menéndez, J. A.; Díez, M. A.; Suárez, D.; Montes-Morán, M. A. *J. Phys. Chem. B* **2003**, *107*, 6350.
- (18) Nakajima, T.; Mabuchi, A.; and Hagiwara, R. *Carbon* **1988**, *26*, 357.
- (19) He, H.; Klinowski, J.; Forster, M.; Lerf, A. *Chem. Phys. Lett.* **1998**, *287*, 53.
- (20) Lerf, A.; He, H.; Forster, M.; Klinowski, J. *J. Phys. Chem. B* **1998**, *102*, 4477.
- (21) McAllister, M. J.; Li, J.-L.; Adamson, D. H.; Schniepp, H. C.; Abdala, A. A.; Liu, J.; Herrera-Alonso, M.; Milius, D. L.; Car, R.; Prud'homme, R. K.; and Aksay, I. A. *Chem. Mater.* **2007**, *19*, 4396.
- (22) Kudin, K. N.; Ozbas, B.; Schniepp, H. C.; Prud'homme, R. K.; Aksay, I. A.; Car, R. *Nano Lett.* **2008**, *8*, 36.
- (23) Li, J.-L.; Kudin, K. N.; McAllister, M. J.; Prud'homme, R. K.; Aksay, I. A.; Car, R. *Phys. Rev. Lett.* **2007**, *96*, 176101.
- (24) Paci, J. Y.; Belytschko, T.; Schatz, G. C. *J. Chem. Phys.* **2007**, *111*, 18099.
- (25) Gilijee, S.; Han, S.; Wang, K. L.; Kaner, R. B. *Nano Lett.* **2007**, *7*, 3394.
- (26) Boukhvalov, D. W.; Katsnelson, M. I.; Lichtenstein, A. I. *Phys. Rev. B* **2008**, *77*, 035427.

- (27) Artacho, E.; Gale, J. D.; Garsia, A.; Junquera, J.; Martin, R. M.; Orejon, P.; Sanchez-Portal, D.; Soler, J. M. SIESTA, Version 1.3, 2004.
- (28) Soler, J. M.; Artacho, E.; Gale, J. D.; Garsia, A.; Junquera, J.; Orejon, P.; Sanchez-Portal, D. *J. Phys.: Condens. Matter* **2002**, *14*, 2745.
- (29) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (30) Monkhorst, H. J.; Park, J. D. *Phys. Rev. B* **1976**, *13*, 5188.
- (31) Yazyev, O. V.; Helm, L. *Phys. Rev. B* **2007**, *75*, 125408.
- (32) Son, Y.-W.; Cohen, M. L.; Loui, S. G. *Nature (London)* **2006**, *444*, 347.
- (33) Wang, W. L.; Meng, S.; Kaxiras, E. *Nano Lett.* **2008**, *8*, 241.
- (34) Janotti, J.; Wei, S.-H.; Singh, D. J. *Phys. Rev. B* **2001**, *64*, 174107.

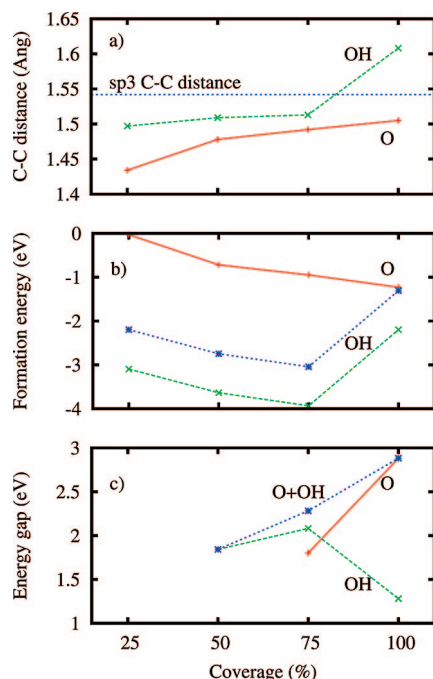


Figure 3. Dependence of carbon–carbon bond length (a), chemisorption energy (b), and electron energy gap (c) on coverage (see the text).

The basis for carbon atoms was optimized as proposed earlier for pure graphite.³⁵

Chemisorption energies were calculated by standard formulas used, e.g., earlier for the case of chemisorption of hydrogen on graphene²⁶ and a solution of carbon in γ -iron.³⁶ Thus, energy of chemisorption of a single oxygen atom at eight carbon atoms (Figure 2a) is calculated as $E_{\text{form}} = E_{\text{C}_8\text{O}} - E_{\text{C}_8} - E_{\text{O}_2}/2$ where $E_{\text{C}_8\text{O}}$ is the total energy of the supercell found by self-consistent calculations after optimization of geometric structure, E_{C_8} is the total energy of graphene supercell, and E_{O_2} is the energy of oxygen molecule. For the case of hydroxyl group, instead of oxygen, its energy was calculated with respect to water in gaseous phase: $E_{\text{OH}} = E_{\text{H}_2\text{O}} - E_{\text{H}_2}/2$. Alternatively, the chemisorption energy can be calculated as $E_{\text{OH}} = E_{\text{H}_2\text{O}}/2 + E_{\text{O}_2}/4$. These two expressions estimate the chemisorption energy from above and from below (see Figure 3b where the results corresponding to the first and to the second expression are shown by dashed green and dotted blue, respectively). To be specific, in further discussions we will use the first estimation (the dashed green line). Actually, the chemisorption energy for GO containing both oxygen and hydroxyl groups depend on its chemical composition. For example, the chemisorption energy of oxygen and the OH group in the system $\text{C}_8(\text{OH})_4\text{O}$ are $E_{\text{chem}} = E_{\text{C}_8(\text{OH})_4} + E_{\text{O}_2}/2 - E_{\text{C}_8(\text{OH})_4\text{O}}$ and $E_{\text{chem}} = (E_{\text{C}_8(\text{OH})_2\text{O}} + 2E_{\text{OH}} - E_{\text{C}_8(\text{OH})_4\text{O}})/2$, respectively.

To check accuracy of the method used, we have calculated formation energy of the water from molecular oxygen and hydrogen in the gaseous phase. We have found the value 213.4 kJ/mol which is rather close to the experimental value 241.8 kJ/mol. Underestimation of the energy by approximately 10% is typical for GGA calculations.³⁶ Also, we have calculated equilibrium interatomic distances for graphene, molecular oxygen, hydrogen, and water, as well as interlayer distances in graphene. When drawing the pictures of density of states, we used a smearing by 0.3 eV.

3. Results and Discussion

We start our simulations with the case of oxygen chemisorption and then consider the chemisorption of hydroxyl groups. Last, we investigate their various combinations. Let us consider first a supercell of graphene containing eight carbon atoms, the chemisorption of two of them corresponding to 25% coverage. In contrast with hydrogen, oxygen forms a bridge between two carbon atoms, as shown in Figure 1a. As well as for the case of hydrogen, the chemisorption leads to distortions of graphene sheets when the atoms coupled to oxygen are shifted up and their neighbors are moved in the opposite direction. This makes chemisorption of the next oxygen atom from the opposite side of graphene sheet the most energetically profitable (Figure 1a). Various oxygen configurations for various coverages are sketched in Figure 2a–e, and the computational results for carbon–carbon distances, chemisorption energies, and electron energy gaps are presented in Figure 3. One can see from Figure 3a that the length of bonds between functionalized carbon atoms grows from the standard value for graphene, 1.42 Å, to the standard value for diamond, 1.54 Å, at the coverage increase which corresponds to the transition from sp^2 to sp^3 hybridization of carbon atoms. The chemisorption energy increases in absolute value with the coverage increase, and the most stable is the configuration displayed in Figure 1a. The gap in electron energy spectrum opens starting from 75% coverage where its value is 1.8 eV; with the coverage increase, it grows up to 2.9 eV.

Hydroxyl groups are bonded with graphene similar to that of hydrogen,²⁶ that is, they sit at neighboring carbon atoms from opposite sides of the graphene sheet (Figure 1b). Distortion of the sheet is stronger in this case than in the case of hydrogen, partially because of interaction between the hydroxyl groups leading to ordering of distortion (see Figure 1b,c). Various calculated configurations are sketched in Figure 2f,g. The chemisorption energy was calculated with respect to water which is probably the most informative to consider reduction of GO. With the coverage increase, the carbon–carbon distance grows, as shown in Figure 3a. For the case of complete coverage it turns out to be larger than a standard one for a single bond (sp^3 hybridization) which means a situation close to a break of the graphene sheet. In contrast with the cases of hydrogen and oxygen, the chemisorption energy is not monotonous as a function of coverage reaching the minimum at 75% which should correspond, therefore, to the most optimal configuration (Figure 1b).

Let us consider now a general case of functionalization of graphene by both hydroxyl groups and oxygen atoms. Typical combinations are shown in Figure 4. Total energy calculations demonstrate that for all the combinations under consideration the chemisorption energy per hydroxyl group is 60 meV lower, and per oxygen atom, 30 meV lower than for the pure cases with the same degrees of coverage. Thus, mixed coverage is energetically favorable in these cases (coverage between 25% and 75%), diminishing the energy of both O and OH groups. For coverage less than 25%, the chemisorption energy for hydroxyl groups turns out to be lower than for oxygen; therefore, one can conclude that GO with 25% coverage contains only OH groups whereas some oxygen atoms can appear only as edge groups. Optimal configurations for 25%, 50%, and 100% coverage are shown in Figures 4a, e and c, and h, respectively. One should stress that a structure with staggered stripes of sp^2 and sp^3 carbon atoms is formed at 50%, in agreement with the previous works.^{21,22} For maximal coverage, as well as for the case of OH groups only, carbon–carbon distances exceed 1.54

(35) Junquera, J.; Paz, O.; Sanchez-Portal, D.; Artacho, E. *Phys. Rev. B* **2001**, *64*, 235111.

(36) Boukhvalov, D. W.; Gornostyrev, Y. N.; Katsnelson, M. I.; Lichtenstein, A. I. *Phys. Rev. Lett.* **2007**, *99*, 247205.

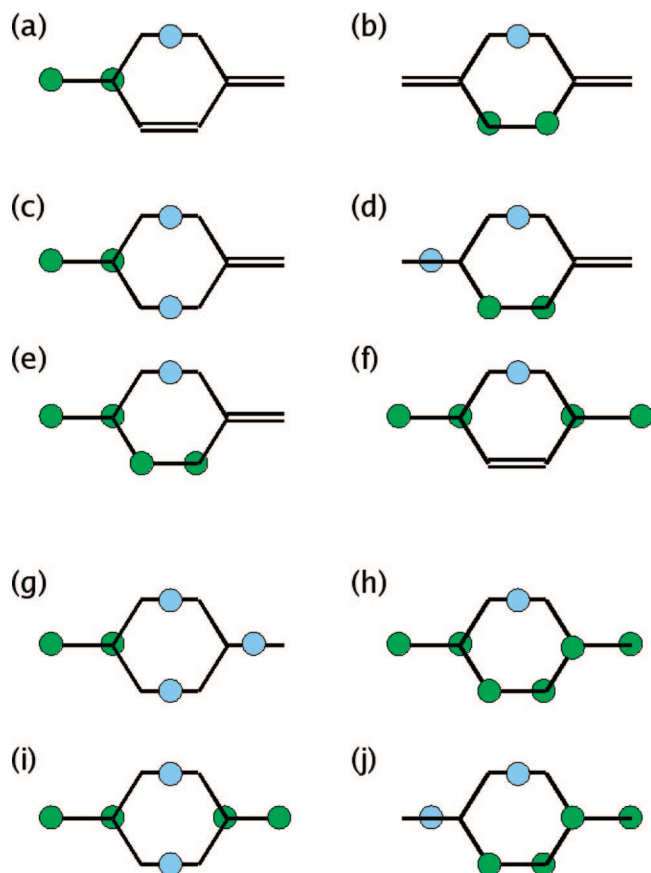


Figure 4. A sketch of functionalization of graphene by oxygens (blue circles) and hydroxyl groups (green circles).

Å which makes, again, 100% coverage less favorable than 75% coverage. The most stable configuration of GO is presented in Figure 1c.

As a result, one can suggest the following chemical formulas for GO with various coverages: 25%, $C_8(OH)_2$; 50%, $C_8(OH)_2O$; 75%, $C_8(OH)_4O$. They are rather close to the formulas suggested by experimentalists and discussed in the Introduction. Minor discrepancies can be related with the presence of some small amount of carboxyl and carbonyl groups, as well as atomic oxygen adsorbed at the edges of GO, as was discussed in detail within the model proposed by Lerf et al.^{19,20}

Electron densities of states for GO are presented in Figure 5. One can see that the energy gap varies between 2.8 and 1.8 eV at the decrease of coverage from 75% to 50%. At further reduction of GO it becomes conducting, according to our calculations. It seems to be in agreement with the available experimental data.^{4,25,37}

The chemisorption energy difference per group for 25% and 75% coverage is less than 1 eV (Figure 3a) which explains a possibility of partial reduction of GO, both thermally and chemically. Actually, the carbon to oxygen ratio 4:1 considered above is a bit larger than experimental values for strongly reduced GO^{14,25,38,39} and almost twice larger than the maximal

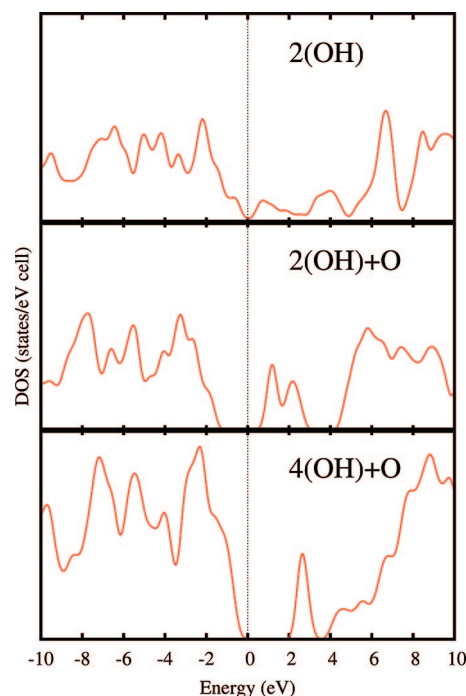


Figure 5. Electronic densities of states for the most stable configurations at various degrees of coverage. Number of hydroxyl groups and oxygen atoms per C_8 is shown.

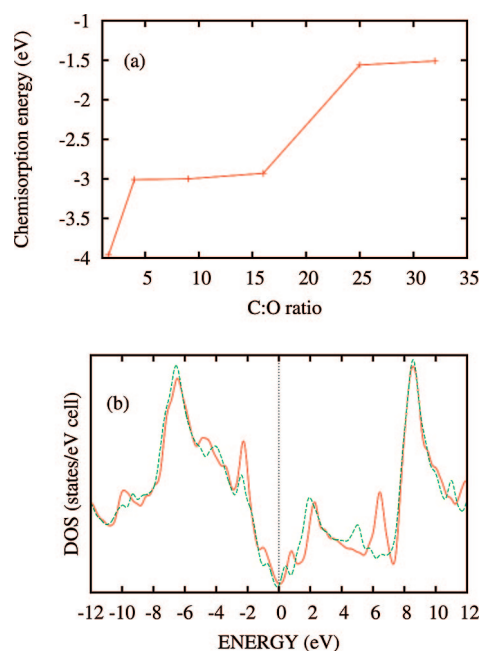


Figure 6. (a) Chemisorption energy of OH groups as a function of C:O ratios. (b) Total densities of states per atom for C:O ratios 16:1 (solid red line) and 32:1 (dashed green line).

ratio 10:1.³⁷ To study dependence of the chemisorption energy on the C:O ratio we have performed calculations for the cases of two hydroxyl groups (see Figure 2f) per supercells containing 8, 18, 32, 50, and 72 carbon atoms, the latter case corresponding to the C:O ratio 32:1. The computational results are presented in Figure 6a. One can see that the chemisorption energy is weakly concentration-dependent between the ratio values 4:1 and 16:1 whereas for smaller concentrations of hydroxyl groups, it decreases roughly twice, between 16:1 and 25:1. A weakening of chemical bonding between OH groups and graphene at small

- (37) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. *Carbon* **2007**, *45*, 1558.
 (38) Bourlinos, A. B.; Gournis, D.; Petridis, D.; Szabó, T.; Szeri, A.; Dékány, I. *Langmuir* **2003**, *19*, 6050.
 (39) Stankovich, S.; Piner, R. D.; Chen, X.; Wu, N.; Nguyen, S. T.; Ruoff, R. S. *J. Mater. Chem.* **2006**, *16*, 155.

concentrations (C:O ratio from 25:1 in comparison with 16:1) is connected with essential changes of the electronic structure. At very small concentrations, the latter is more similar to that of pure graphene (see Figure 6b). It can be caused by the changes of distances between OH groups which is 17 Å for the carbon-to-oxygen ratio 16:1. It was shown at the simulation of hydrogenization of graphene²⁶ that typical radius of interaction between the hydrogen atoms is about 8 Å, and the defects can be considered as independent ones for larger distances. For the case of OH groups, the distortions of the graphene sheet is larger than for the case of hydrogen, and therefore interaction between them is still essential for the ratio 16:1 whereas for smaller concentrations, the hydroxyl groups can be considered as almost noninteracting. In a real experimental situation where the ratio 10:1 has been reached³⁷ finite-size effects of the GO flakes can be important. Indeed, the size of these flakes is smaller than for the case of graphene,^{9,23} and various groups can be chemisorbed at the edges. Also, the flakes can contain various topological defects^{10,23} which can also change local chemisorption energy.

At last, let us discuss the cases of bilayer and periodic (graphite-like) GO. To this aim we have carried out calculations for corresponding structures with 25% coverage by hydroxyl groups. We consider the Bernal (AB) stacking, similar to pure graphite, which was observed also in GO.¹⁶ The optimized structure is shown in Figure 7. The width of the layer was found to be, in both cases, about 7 Å, as well as interlayer distances, which seems to be in a good agreement with experimental data.^{38,40,41} To calculate interlayer coupling energy per carbon atom we have computed the energy differences between single layer and periodic structure. For the case of pure graphite, it equals 32 meV, in a good agreement with the experimental value 35 meV.⁴² For the periodic GO structure and for GO bilayer, the corresponding values turn out to be 17 and 6 meV, respectively. This decrease of the energy explains possibility of easy exfoliation in GO.^{9,10} Because of weakness in the interlayer coupling, the electronic structure of GO is almost identical for single layer, bilayer, and periodic structure, in contrast with the cases of pure graphene.⁴³

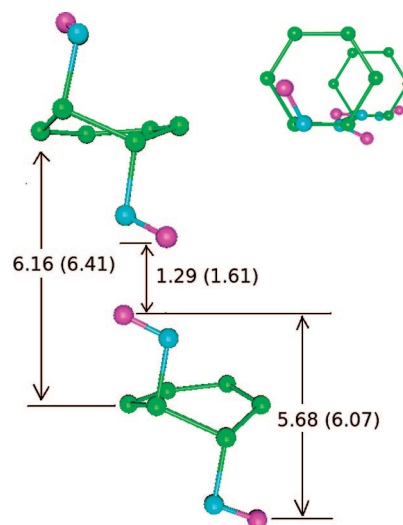


Figure 7. Optimized geometric structures of strongly reduced GO. Numbers are distances, in Å, for the periodic structure (and for bilayer in parentheses). Right upper corner: a top view. Carbon, oxygen, and hydrogen atoms are shown in green, blue, and violet, respectively.

4. Conclusion

To summarize, we have proposed a model structure of GO which seems to be consistent with all known experimental data. We have demonstrated, in particular, that (i) 100% coverage of GO is less energetically favorable than 75%, (ii) functionalization by both oxygen and hydroxyl groups is more favorable for coverage than 25% than by hydroxyl groups only, (iii) a reduction of GO from 75% to 6.25% (C:O ratio 16:1) coverage is relatively easy but further reduction seems to be rather difficult, and (iv) GO becomes conducting at 25% coverage, being an insulator at larger coverage.

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Supporting Information Available: Cartesian coordinates for all species, and values of calculated formation energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(40) Dékány, I.; Krüger-Grasser, R.; Weiss, A. *Colloid Polym. Sci.* **1998**, 276, 570.

(41) Kovtykhova, N. I.; Olliver, P. J.; Martin, B. R.; Mallok, T. E.; Chizhik, S. A.; Buzaneva, E. V.; Gorchinskiy, A. D. *Chem. Mater.* **1999**, 11, 771.

(42) Benedict, L. X.; Chopra, N. G.; Cohen, M. L.; Zettl, A.; Loui, S. G.; Crespi, V. G. *Chem. Phys. Lett.* **1998**, 286, 490.

(43) Boukhvalov, D. W.; Katsnelson, M. I. *Phys. Rev. B*, submitted, cond-mat:0802.4256.