

■ Electro, Physical & Theoretical Chemistry

Atomic Transport at Charged Graphene: Why Hydrogen and Oxygen Are So Different

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Atoms on charged graphitic carbon surface are relevant to various electrochemical problems, understanding the adsorption and diffusion of adatoms under charging conditions is essential towards using graphene-like materials in electrochemistry. Using density functional calculations, we show that electron or hole doped graphene can strongly change the mobility of H and O adsorbed atoms. Interestingly, charge doping affects the diffusion of H and O in opposite ways, namely, electron doping increases/reduces, while hole doping reduces/increases the diffusion barrier of H/O respectively. Specifically, on neutral graphene the diffusion barriers of H and

O are 1.01 and 0.74 eV, which are, upon a hole doping level of $+5.9 \times 10^{13} \text{ cm}^{-2}$, 0.77 and 0.90 eV, and upon an electron doping level of $-5.9 \times 10^{13} \text{ cm}^{-2}$, 1.36 and 0.38 eV. Thus, within the harmonic transition state theory, at room temperature, the diffusion rate of O can be decreased or increased by 470 or 1×10^6 times, while that of H can be increased or decreased by 1×10^4 or 7×10^5 times, respectively for the above hole or electron doping density. The difference between H and O atomic transport at charged graphene is interpreted in terms of the difference in geometric and bonding changes upon charge doping.

Introduction

Interactions between the adatoms and graphene are of much studied topics.^[1–5] Fundamentally, besides the stability of the adsorbed atoms or molecules, their dynamics under certain conditions is also a non-trivial facet that needs to fully be taken into account towards realistic applications. There are several factors that largely influence the diffusion of an adsorbate on graphitic support, including contact with solid surfaces,^[6,7] co-adsorption,^[4,8,9] lattice strain,^[10] and charge doping.^[2,11,12] The latter is practically important in understanding mechanisms of electrochemical reactions as graphene and related materials have been widely used in electrochemical problems.^[13]

In this work, based on density-functional calculations, we present a detailed study on the stability and mobility of O and H atoms on charged graphene. Oxygen and hydrogen are much related to electrochemical oxidation and hydrogenation processes. Additionally, hydrogenated graphene or graphene oxide materials are very commonly used in electrochemistry.^[14,15] We shall show that electron/hole doping affects the adsorption of H and O in opposite ways, and analyze the origins of this difference.

Methods

Technically, a graphene unit cell of 4×4 periodicity was adopted, with a vacuum layer of 16 Å separating graphene sheet images. Our calculations show that the difference between 4×4 and 8×8 unit cells in the adsorption of H is fully negligible. Specifically, the adsorption energy of H changes by 3 meV, and the CH bondlength changes by less than 0.001 Å. We are thus confident that the 4×4 periodicity is large enough to minimize the interaction of the adsorbates and their periodic images. We conducted spin-polarized plane-wave density-functional calculations using the PBE functional,^[16] and ultrasoft pseudopotentials,^[17] as encoded in the Quantum ESPRESSO package.^[18] A kinetic cutoff of 40 Ry was applied. The charge analysis method proposed by Bader was adopted.^[19] A 3×3 k-point grid was chosen to sample the Brillouin zone in self-consistent calculations. A denser k-point grid of 8×8 was used for electronic density of states analyses.^[20] Electron or hole doping was simulated by adding or removing an amount of electrons, and technically this was counterbalanced by the same amount of opposite sign background charges to avoid the total energy divergence. For instance, adding 0.5 holes to the unit cell corresponded to a doping level of $+5.9 \times 10^{13} \text{ cm}^{-2}$. Although we are not able to directly quantitatively compare our results from this charge approach with experiments our calculations do capture the essentials of graphene under charging, that is, the Dirac point is shifted up/down with respect to the Fermi level under the hole/electron doping condition. Diffusion barriers were determined by the so-called climbing image nudged elastic band methods,^[21] with 9 images in each band. Force convergence thresholds of 10^{-3} and 10^{-4} au were applied in geometry and band optimization, respectively. The binding energy of H or O with graphene is given by $\Delta E_b = E(*X) - E(X)$ ($X=H,O$), where $E(*X)$ and $E(X)$ are the total

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energy respectively when X is adsorbed on graphene or placed amid the vacuum layer.

Results and Discussion

H, as a monovalent species, is most stabilized at an on-top site (above a C atom) of graphene.^[4,8] O, on the other hand, is found to be more stable at a bridge site (above the middle point of a CC bond).^[6] Upon H or O adsorption, the initial sp^2 hybridization of its bonding partners is transferred to the sp^3 hybridization. In this work the diffusion of H or O is a process in which H or O jumps from one adsorption site to an adjacent equivalent, as in the inset of Figure 1(a) and Figure 2(a). In

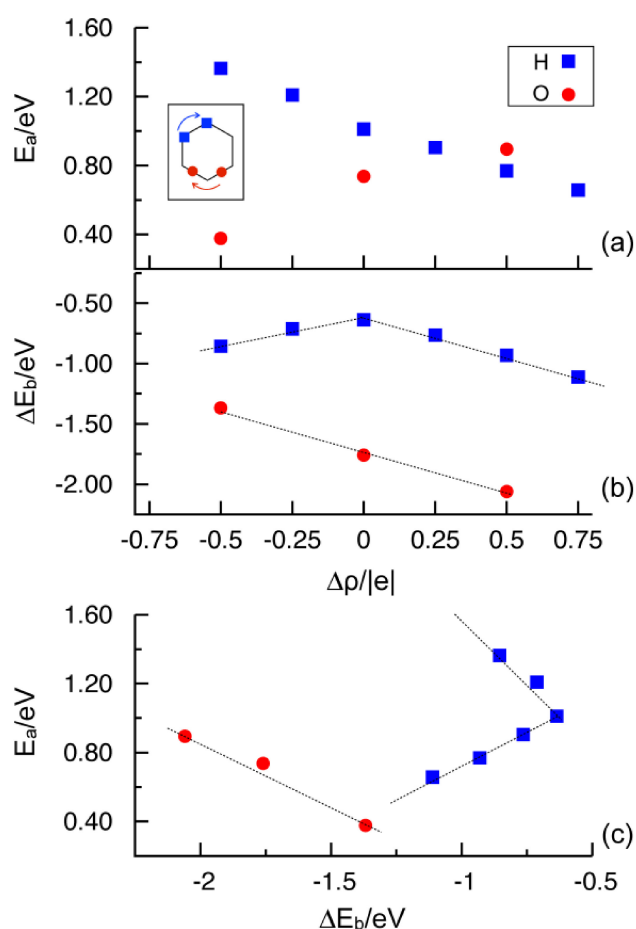


Figure 1. Diffusion energy barrier E_a (a) and binding energy ΔE_b (b) against the charge doping level, E_a against ΔE_b (c).

Figure 1(a) we show the diffusion energy barriers of H and O on graphene against the charge doping level, amount of charge $\Delta\rho$ added to the unit cell. In agreement with a previous theoretical study,^[2] our calculations predict that electron doping lowers, while hole doping increases, the energy barrier for O diffusion. It is also in agreement with the other works^[2,10] that estimated a barrier of 0.74 eV in the case of neutral unit

cell. The doping of 0.5 electrons leads to a barrier of 0.38 eV, and the doping of 0.5 holes leads to a barrier of 0.90 eV.

The graph clearly suggests an opposite trend for H diffusion, that is, electron doping increases while hole doping decreases the barrier. Similar to previous studies,^[4] without charge doping, the diffusion energy barrier of H is calculated to be 1.01 eV. We determined the diffusion process of H for various charge doping densities, equivalent to 0.50, 0.25 electrons, and 0.25, 0.50, 0.75 holes added to the unit cell. The diffusion barrier is 1.36, 1.21, 0.90, 0.77, 0.65 eV, respectively. The change in diffusion barrier with respect to the charge doping level here leads to interesting implications. Within the harmonic transition state theory, the diffusion rate is given by Vineyard's equation $k = \nu_0 e^{-E_a/k_B T}$,^[22] where the prefactor ν_0 is assumed to be the same for all charge doping levels in this work. Thus, at room temperature the diffusion rate of H can be increased or decreased by 1×10^4 or 7×10^5 times, and that of O can be decreased or increased by 470 or 1×10^6 times, by adding 0.5 holes or electrons to the unit cell, respectively. Figure 1(b) shows the binding energy against the charge doping level. While the binding energy of O is smaller (closer to zero) against electron doping, and larger against hole doping, the binding energy of H is larger against both electron and hole doping. Figure 1(c) indicates that O on graphene obeys the Brønsted-Evans-Polanyi principle, which suggests a linear relationship between the diffusion barrier on a surface of an adsorbed species and its surface binding energy,^[23] hence the stronger the O-graphene binding is, the higher diffusion barrier would be. For H, this only holds for electron doping, and becomes violated for hole doping.

To provide insights into the difference between the O and H adsorption cases above, we first examine structural properties of the initial state (IS) and transition state (TS) shown in Figure 2(a). In the IS, as in Figure 2(b,c), the CH bond length, which is minimal at zero charge doping, is slightly changed upon charge doping, while the CO bond become considerably elongated/shortened with electron/hole doping. In particular, within $(-0.75, +0.75)$ |e| doping range, the CH bond length variation is 0.006 Å, which is about an order smaller than that of the CO bond, 0.042 Å. The bond length changes suggest that the local CH bonding might not really be affected by charge doping, while the CO bond is strengthened by hole doping and weakened by electron doping. In the TS, on the other hand, Figs. 2(d,e) indicates that the CO bond is slightly increased, from 1.410 to 1.422 Å, while the CH bonds are largely decreased from 1.366 to 1.325 Å, when the doping level changes from -0.5 to $+0.5$ |e|, respectively.

How does the vicinity of H or O on the graphene surface react to charge doping? Figure 2(f) shows the bond length of the C bonding partner of H and its neighboring C atoms, and Figure 2(g) shows that of the two C bonding partners of O, in the IS. In the case of H adsorption, the CC bond length is decreased from 1.503 Å (-0.5 |e| doping) to 1.492 Å ($+0.5$ |e| doping) whereas in the case of O adsorption, the CC bond length is increased from 1.494 Å to 1.514 Å. That result means electron doping enhances or reduces, while hole doping reduces or enhances, the CC bonding upon O or H adsorption.

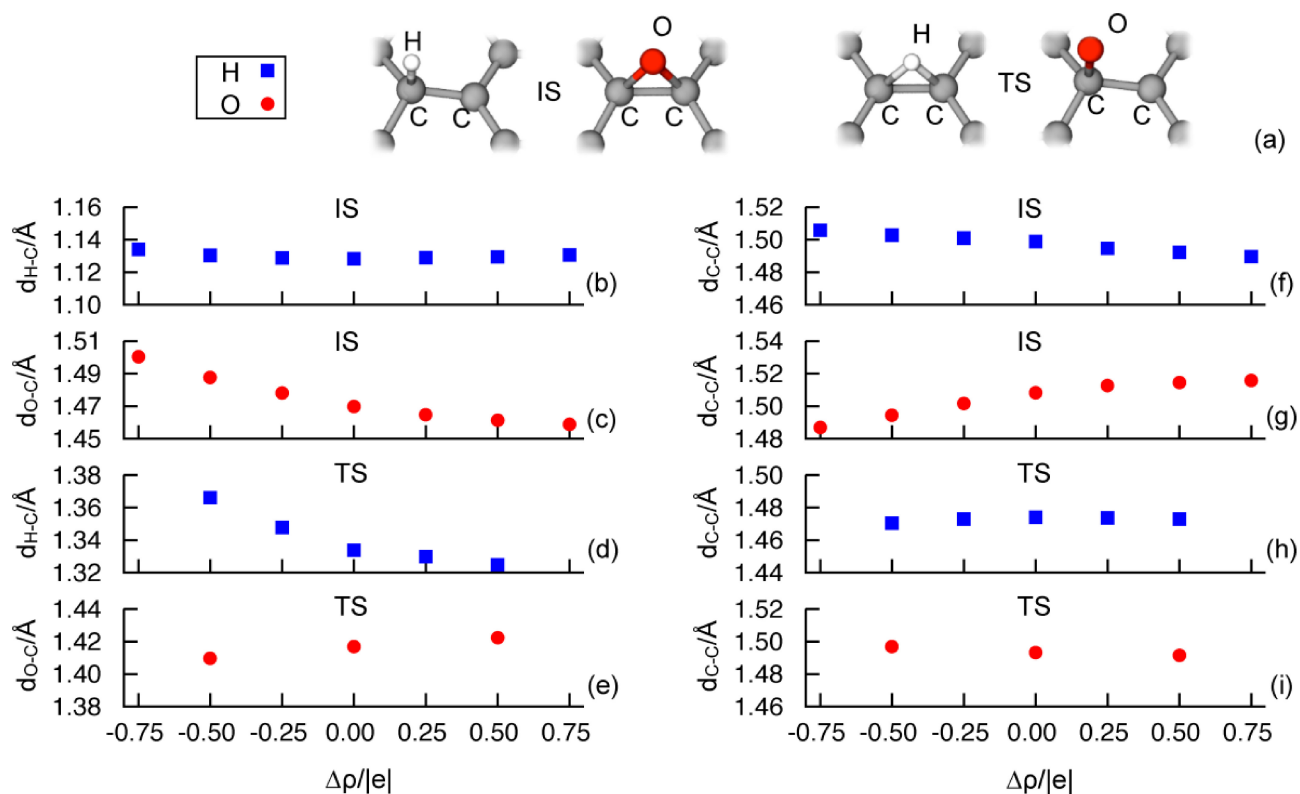


Figure 2. Properties against the amount of charge $\Delta\rho$ added to the unit cell: (a) The migration of a H/O atom from an on-top/bridge site to a neighboring site on graphene; (b) and (c) CH and CO bondlengths in the IS, (d) and (e) that in the TS; (f) and (g) the CC bondlength in the IS of H and O diffusion respectively, (h) and (i) that in the TS.

Note that in the TS the result seems opposite. Although data plotted in Figure 2(h,i) implies a little change in the CC bondlength against the doping level, the CC bond is shortened/elongated for hole/electron doping in the case of O diffusion, while it is maximized for zero charge doping in the case of H diffusion.

To this end, in the case of O, there is a clear correlation in the bondlength between the CO and CC bonds, in both the IS and TS, namely the former is reduced while the latter is increased, and vice versa, upon charge doping. No such clear correlation between the CH and CC bonds was found, in both the IS and TS, namely if the CH bondlength varies strongly the CC one just slightly changes, and vice versa, upon charge doping. From the geometry considerations, the energy barrier reduction/increase in the case of O upon electron/hole doping is a result of the weakening/strengthening of the CO bond in the IS and its strengthening/weakening in the TS. For H, seemingly, only the weakening/strengthening of the CH bond in the TS caused by electron/hole doping leads to the increase/reduction of the diffusion barrier.

How geometric properties presented above correlated with electronic properties? Figure 3(a,b) show the projected density of states (PDOS) of H on graphene, in the IS and TS structures. As indicated by previous studies,^[1,3,4] the adsorption of a H atom leads to an energy gap caused by H^+ ionic core potential^[1,4] in the energy spectrum of graphene. This is

demonstrated with Figure 3(a). Note that upon H adsorption a $2p_z$ electron of the carbon lattice is unpaired, resulting in unequal numbers of $2p_z$ electrons available in the sublattices A and B of graphene. Therefore, there exists an occupied spin-up and unoccupied spin-down gap state, Figure 3(a), and the system thus carries a magnetic moment of $1 \mu_B$. From a chemical point of view, this unpaired electron destabilizes the graphene lattice since it locally contravenes Hückel's rule. In the TS, Figure 3(b), the PDOS shows that a Dirac-like point appears at an energy 0.9 eV below the Fermi level. Importantly, no magnetic moment was found in this structure because the H-1 s electron interacts with both $2p_z$ electrons of the two C atoms nearby. Note that there are sharp peaks of H-1 s PDOS at 0.4 eV above the Fermi level, associated with antibonding states between H and the two C atoms. A charge analysis predicts the H atom in the IS and TS geometries is charged by 0.06 and 0.18 $|e|$, respectively. This implies that the ionic character is increasingly important in the TS of H diffusion.

Charge doping leads to similar PDOS, however, it shifts the electronic levels to different energies compared to the Fermi level. In the IS, for example, 0.5 $|e|$ doping changes spin-up gap state from fully occupied to partly occupied (Figure 3(c)), while $-0.5 |e|$ doping changes the spin-down gap state from unoccupied to partly occupied (Figure 3(e)). Consistently, the magnetic moment in the unit cell is now reduced to $0.5 \mu_B$ in both cases. Charge doping in this case is clearly a way to

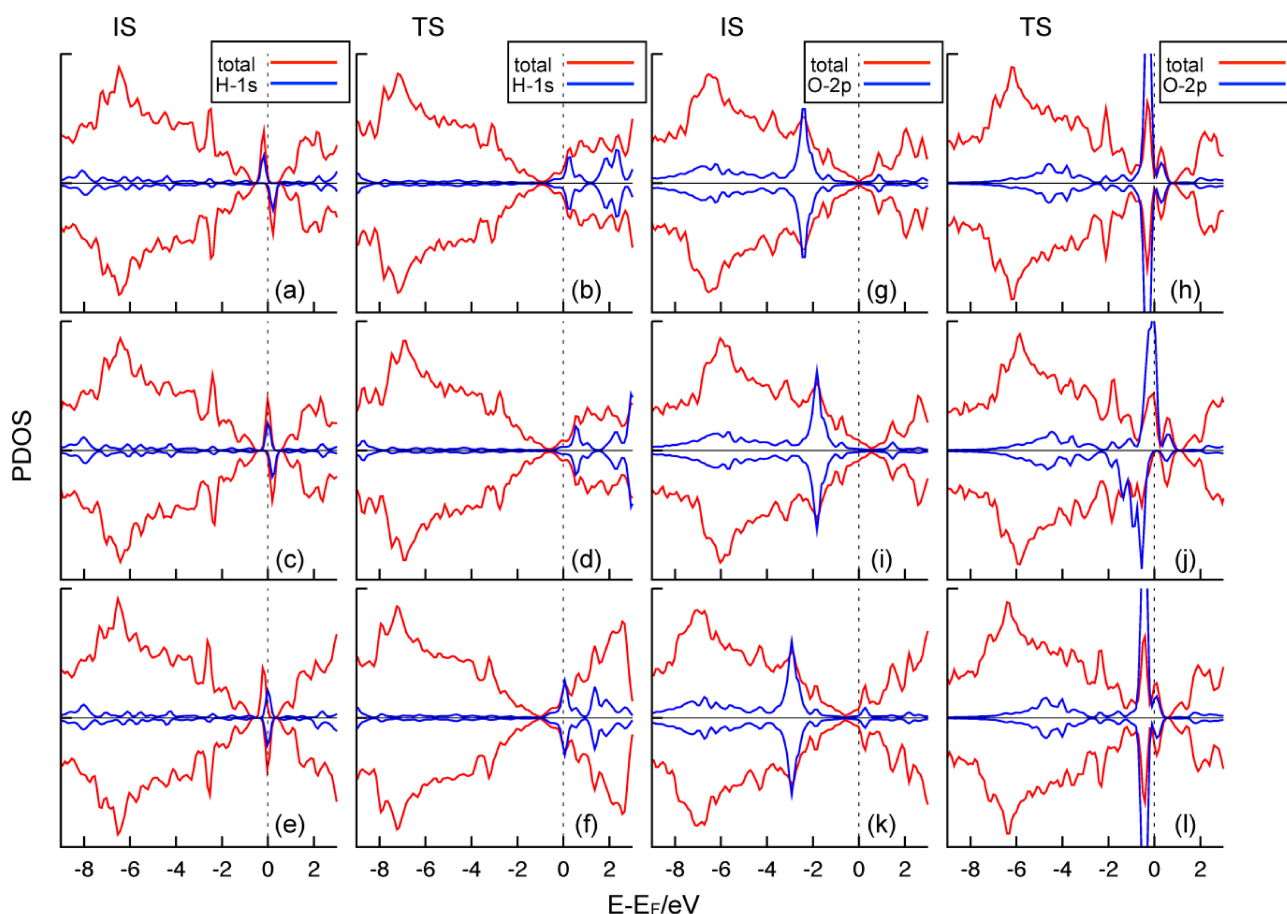


Figure 3. Density of states: (a,b,g,h) no charge doping, (c,d,i,j) 0.5 |e| added to the unit cell, (e,f,k,l) -0.5 |e| added to the unit cell; (a,c,e) IS of H on graphene, (b,d,f) TS of H on graphene, (g,i,k) IS of O on graphene, and (h,j,l) TS of O on graphene. The H-1 s PDOS is scaled by 8 times and O-2p PDOS is scaled by 4 times.

“remove” unpaired electrons from the system, strengthening interatomic bonding in the graphene lattice and then lowering the reactivity of this lattice to H. This is a reason why the CH bond is (slightly) longer upon charge doping. Note, however, that a somewhat longer CH bond upon charge doping does not mean H binds less strongly to the carbon lattice, as Figure 1(b) suggests the opposite. When H and graphene are apart, both hole and electron doping reduces the bond order of the CC bonds hence weakening the CC bonding, when H and graphene are bound, both hole and electron doping reduces the unpaired electron effect, enhancing the CC bonding. Thus an overall result is that charge doping stabilizes H on graphene. The adsorption of H on graphene therefore cannot fully be described by local interactions between H and a C atom since it is a collective process involving delocalized $2p_z$ electrons.^[3] PDOS shifting to the higher or lower energies upon hole or electron doping is also found in the TS, see Figure 3(d,f). Note that electron doping makes the antibonding states right above the Fermi level occupied, see Figs. 3(b) and (f), thereby weakening the CH bonds.

To have a clearer picture of where the additional electrons and holes located we calculated the electron or hole addition

density by $\Delta\rho_{\text{ele/hole}}(\mathbf{r}) = \rho^{-/+}(\mathbf{r}) - \rho^0(\mathbf{r})$, where $\rho^{-/+}(\mathbf{r})$, $\rho^0(\mathbf{r})$ are the electron density of $-/+0.5|e|$ and zero charged systems, all calculated in the zero charged geometries. As indicated by Figure 4(a), in the IS, the added electrons or holes are mainly

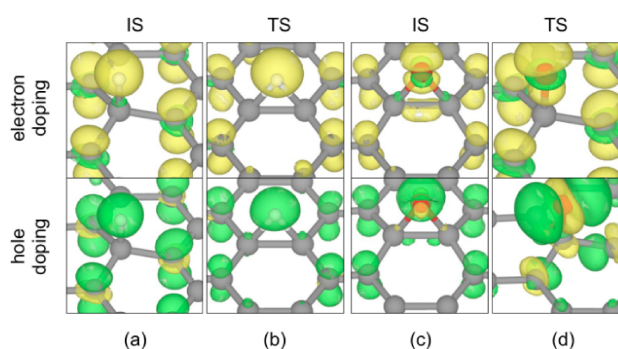


Figure 4. Added electron (in yellow) and hole (in green) densities, where the isosurface value is set at 0.001 au, for: (a) and (b) H on graphene in the IS and TS; (c) and (d) O on graphene in the IS and TS.

associated with the 1 *s* orbital of H and 2*p_z* orbitals of C atoms surrounding the CH bond (we called these C atoms C₃). We found that upon electron or hole doping, there is an electron depletion or accumulation in the *sp*² orbitals of C₃, that may reduce or enhance the bonding between C₃ and the C atom bound to H, consistent with the increase or decrease in the bondlength shown in Figure 2(f). We found a small electron depletion above the C atom in the CH bond upon electron doping, and this may explain a slight elongation of this bond, Figure 2(b). Upon hole doping the CH bond is also elongated, Figure 2(b), and the reason could be that, the CH bond order is decreased as there is a certain amount of H-1 *s* electron is removed. In the TS, added electrons or holes are also associated with the H-1 *s* and C₃-2*p_z* orbitals. Note that, as mentioned above, the ionic polarization stabilizes the CH bonds in the TS, added electrons or holes will reduce or enhance this polarization, then, weaken or strengthen the CH bonds, thereby increasing or decreasing their length, Figure 2 (d).

Clearly, both occupied and unoccupied states are made mainly up by the C₃-2*p_z* orbitals, and little by H-1 *s* orbital (see also, Figure 3(a)). This may explain why adding holes or electrons only slightly changes the CH bondlength (see Figure 2(b)), but much more strongly influences the CC bond (see Figure 2(f)). Hole doping reduces the repulsion between these C atoms caused by the interactions between the *sp*₃ (of C bound to H) and 2*p_z* (of C₃), thereby reducing the CC bondlength, as indicated in Figure 2(f).

We now analyze the PDOS in the case of O. In the IS, differently from the result for H on graphene, the PDOS of O on graphene in the IS shows no bandgap, Figure 3(g). The hybridization of O-2*p_z* and C-2*p_z* results in bonding states lying below, and antibonding states above the Fermi level. Adding electrons or holes shifts electronic energy levels to the left or the right of the Fermi level, Figure 3(i,k), making them occupied or empty. The result is supported with Figure 4(c), and upon electron or hole doping, there is a small depletion or accumulation of electron above the two C atoms bound to O. This gives an idea why CO bond is weakened by electron doping and strengthened by hole doping. The result also leads to the strengthening and weakening of the CC bonds, upon charge doping, as indicated in Figure 2(g), and also explains the stability of O on graphene against doping, Figure 1(b). For the TS, the PDOS exhibits very sharp peaks right below the Fermi level, which show more O-2*p_z*, 2*p_y* characters, and lower peaks right above the Fermi level, which are associated with O-2*p_z* orbitals, Figs. 3 (h) and 4(d). Hole doping makes the sharp peaks partly occupied, Figure 3(j), that destabilizes the CO bond. Moreover, there is an electron depletion or accumulation in the CC bonds upon electron or hole doping. This is an interpretation of why the CO or CC bond is shortened or elongated by electron doping, and vice versa. Finally, from a charge analysis, the O atom is charged by -0.85 |*e*| in the IS and -1.22 |*e*| in the TS. This shows that ionic polarization is increasingly important for the CO bond in the TS. Electron or hole doping will increase or decrease the polarization, strengthening or weakening the CO

bond in the TS. This is also a reason why electron or hole doping reduces or increases the energy barrier of O diffusion.

We now comment on how charging regimes would affect the performance of graphene as an electrode. Negatively charging means graphene acts as a cathode, at which reduction processes take place. In practice, graphene-based catalysts have been much used in the hydrogen evolution reaction.^[24,25] Fundamentally, the recombination step (Tafel reaction) of two adsorbed H to form molecular hydrogen can be involved, H* + H* → H₂.^[24] Of course, in this reaction the diffusion of adsorbed H should not be overlooked. The electron doping reduced mobility of H is clearly consistent with high efficiency of the use of graphene in such practical applications. Moreover, the weakening of CH bonds upon charge doping also indicates that the formation of molecular hydrogen will thermodynamically be more favorable. In practice, graphene oxide-based complexes have been used as anode materials.^[26,27] Clearly, when these materials operate under charging conditions, the stability of graphene oxide as well as metal oxide is an issue that needs to be addressed. As indicated above, the hole doping stabilizes oxygen atoms on graphene, and reduces their mobility. This means that due to their charge-enhanced stability, graphene oxides are suitable for anode materials. Although, in a realistic electrochemical system (i) an applied electrode potential may result in a quite non-linear charge separation within the double layer, and (ii) electrolyte, temperature and entropy factors can affect the diffusion of hydrogen and oxygen, our study provides some possible insights into such systems based on graphene.

Conclusions

In summary, we have carried out a density-functional study on how charge doping affects the bonding and diffusion of H and O adsorbed on graphene. Electron doping increases while hole doping reduces H diffusion barrier on graphene. Charge doping affects O diffusion on graphene in the opposite way. The difference has been explained by analyses on geometric and electronic properties of the adsorbed system. This may be helpful for understanding electrochemical oxidation or hydrogenation processes based on graphene catalysts.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Density Functional Theory · Doped graphene · Hydrogen and Oxygen · Adsorption · Diffusion

- [1] E. Duplock, M. Scheffler, P. Lindan, *Phys. Rev. Lett.* **2004**, *92*, 225502.
- [2] A. Suarez, L. Radovic, E. Bar-Ziv, J. Sofo, *Phys. Rev. Lett.* **2011**, *106*, 146802.
- [3] S. Casolo, O. Løvvik, R. Martinazzo, G. Tantardini, *J. Chem. Phys.* **2009**, *130*, 054704.
- [4] M.-T. Nguyen, P. N. Phong, N. D. Tuyen, *ChemPhysChem* **2015**, *16*, 1733–1738.
- [5] J. Ito, J. Nakamura, A. Natori, *J. Appl. Phys.* **2008**, *103*, 113712.
- [6] M.-T. Nguyen, *J. Appl. Phys.* **2013**, *113*, 114307.
- [7] M.-T. Nguyen, R. Gebauer, *J. Phys. Chem. C* **2014**, *118*, 8455–8461.

- [8] R. Erni, M. Rossell, M.-T. Nguyen, S. Blankenburg, D. Passerone, P. Hartel, N. Alem, K. Erickson, W. Gannett, Alex Zettl, *Phys. Rev. B* **2010**, *82*, 165443.
- [9] M.-T. Nguyen, R. Erni, D. Passerone, *Phys. Rev. B* **2012**, *86*, 115406.
- [10] M.-T. Nguyen, *J. Phys.: Condens. Matter* **2013**, *25*, 395301.
- [11] L. F. Huang, M. Y. Ni, G. R. Zhang, W. H. Zhou, Y. G. Li, X. H. Zheng, Z. Zeng, *J. Chem. Phys.* **2011**, *135*, 064705.
- [12] R. M. Guzmán-Arellano, A. D. Hernández-Nieves, C. A. Balseiro, G. Usaj, *Appl. Phys. Lett.* **2014**, *105*, 121606.
- [13] A. Ambrosi, C.K. Chua, A. Bonanni, M. Pumera, *Chem. Rev.* **2014**, *114*, 7150–7188.
- [14] O. Jankovský, A. Libánská, D. Bouša, D. Sedmidubský, S. Matějková, Z. Sofer, *Chem. Euro. J.* **2016**, *22*, 8627–8634.
- [15] D. Chen, H. Feng, J. Li, *Chem. Rev.* **2012**, *112*, 6027–6053.
- [16] J. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [17] D. Vanderbilt, *Phys. Rev. B* **1990**, *41*, 7892–7895.
- [18] P. Giannozzi, et al., *J. Phys.: Condens. Matter* **2009**, *21*, 395502.
- [19] a) R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**. b) W. Tang, E. Sanville, G. Henkelman, *J. Phys.: Condens. Matter* **2009**, *21*, 084204. <http://theory.cm.utexas.edu/bader/>.
- [20] We used a smearing scheme with the degauss set at 0.01 Ry.
- [21] G. Henkelman, B. P. Uberuaga, H. Jónsson, *J. Chem. Phys.* **2000**, *113*, 9901–9904.
- [22] A.F. Voter, F. Montalenti, T. C. Germann, *Annu. Rev. Mater. Res.* **2002**, *32*, 321–346.
- [23] R. A. van Santen, M. Neurock, S. G. Shetty, *Chem. Rev.* **2010**, *110*, 2005–2048.
- [24] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, *J. Am. Chem. Soc.* **2011**, *133*, 7296–7299.
- [25] S. S. J. Aravind, M. Costa, V. Pereira, A. Mugweru, K. Ramanujachary, T. D. Vaden, *Int. J. Hydrogen Energy* **2014**, *39*, 11528–11536.
- [26] S. K. Marka, S. Petnikota, V. Srikanth, M. V. Reddy, S. Adams, B. Chowdari, *RSC Adv.* **2016**, *6*, 55167–55175.
- [27] F. Meng, J. Li, S. K. Cushing, J. Bright, M. Zhi, J. D. Rowley, Z. Hong, A. Manivannan, A. D. Bristow, N. Wu, *ACS Catal.* **2013**, *3*, 746–751.

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