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Title: Anomalous stability of graphene containing defects covered by a water layer

The background shows a water layer on the graphene containing Stone–Wales and double vacancy defects. The structural and electronic properties of the systems have been studied by density functional tight-binding method, to understand graphene's stable electronic characteristics.

As featured in:

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Anomalous stability of graphene containing defects covered by a water layer†

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Defects are inevitably present in graphene and can alter its properties and thus its applications. Interestingly, we find that commonly observed Stone–Wales and double vacancy defects do not affect graphene’s hydrophilic and hydrophobic properties and that an adsorbed single water layer does not noticeably affect the defect-containing graphene’s electronic properties. Our findings are based on calculations using a density functional tight-binding theory. Specifically, we observe negligible alteration in the interaction strength (less than 0.1 kcal mol⁻¹) between a single water layer and graphene upon the incorporation of the various types of defects, which indicates that graphene has relatively stable hydrophilic and hydrophobic properties. The presence of a single water layer causes only negligible changes in the energy gap and a small charge transfer to the aqueous layer (less than 0.1 e). The results indicate that the electronic properties of graphene are determined mainly by its own structural characteristics and are not considerably affected by the adsorbed water layer. Further electron structure analysis reveals that the two commonly observed defects do not change the sp² hybridization characteristics of the C atoms of graphene even in the water environment. Our results are significant for graphene studies and applications in areas such as life sciences and materials science where hydrophilic and hydrophobic properties and electronic properties are important.

Introduction

Graphene is known to have many excellent properties, including hydrophilic and hydrophobic properties which are less explored but important in determining its electronic properties and thus its applications in life sciences and materials science; these particular properties have attracted recently a great deal of attention in the scientific community. It has been confirmed that perfect graphene has hydrophobic properties. Studies on graphene adsorbed with water clusters with different numbers of water molecules (n ≤ 6) and water molecule adsorption at different temperatures, including room temperature, have shown that the cluster structure has little effect on the electronic structures. As shown in simulations using Monte Carlo and first-principles theory methods, the structural properties of graphene can be changed by adding external –OH and –COOH functional groups, allowing the enhanced adsorption of small-sized water clusters. The electron mobility of graphene adsorbed with water can be altered by substrate (such as SiO₂) doping, as revealed in both experimental and theoretical studies.

Studies have been conducted on the adsorption of individual water molecules near double vacancy defects and water vapor molecules in the vicinity of crystal defects. However, no research has been reported for water layers on graphene, which means that there is no accurate interpretation of the effect of defects on its hydrophilic and hydrophobic properties. Moreover, it is well known that defects are inevitably present in graphene structures under the impact of the growth environment and external irradiation, and the formation of graphene with sp² hybridization in a real environment could easily involve a variety of defects. Thus, the study of the effect of defects in graphene on its properties, including the impact of the defect structure on its hydrophilic and hydrophobic properties as well as its electronic properties, is urgently needed for its possible application and is thus worthy of further systematic investigations. Stone–Wales defects and double vacancy defects are very common defect types in graphene, and they retain the sp² hybridization characteristics of carbon atoms. At present, there has still been no report on the surface defects of graphene in relation to their impact on its hydrophilic, hydrophobic, and electronic properties. Moreover, due to the limitations of the

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computational methods based on conventional quantum first principles, theoretical calculations can generally only handle some small-scale systems for conformation optimization\textsuperscript{33,54,47} to obtain adsorption-related structural and electronic properties. The consumption of computing resources makes it difficult to conduct a long-timescale simulation and thus limits the effective and reliable description of the hydrogen bonding structure. Classical molecular dynamics methods can achieve simulations for more than nanoseconds (ns) but generally cannot include electronic characteristics in their dynamics simulation, especially in the dynamic process and the electronic structure changes induced due to the change in geometric structure. Thus, it is especially critical to choose a more appropriate method to simulate the adsorption of water molecules on the surface of the material system over a long timescale with the inclusion of electronic information.

**Computational methods**

The recently developed quantum approximate density functional tight-binding (DFTB) method,\textsuperscript{40–44} which is a tight-binding method based on density functional theory (DFT), has greatly improved the size of the simulation system, with a performance almost $10^3$–$10^4$ times faster than that of conventional DFT, while still maintaining the high accuracy of a DFT calculation. It can be used to conduct both large-size, long-time molecular dynamics simulations and accurate analyses of electronic properties. In the recently developed third generation of the DFTB methodology (DFTB3),\textsuperscript{42} the DFTB method based on Hubbard derivatives for the third-order extension\textsuperscript{41} of the SCC-DFTB\textsuperscript{48} includes the $\gamma$ functions and the Hubbard parameters for hydrogen atoms,\textsuperscript{44–46} which is more suitable for systems containing hydrogen bonds such as water.\textsuperscript{46} Considering the effect of the hydrogen bonds of the aqueous system, we use Hubbard derivatives (C: 0.23, O: 0.19, H: 0.16). In this work, we perform molecular dynamics simulations of perfect and defective graphene covered with a single water layer using the DFTB3 method, and the equations of motion of nuclei were integrated using the Velocity–Verlet algorithm\textsuperscript{45} with an NVT ensemble via Andersen thermostat\textsuperscript{46} in the MD simulations, aiming to reveal the effects of the type and density of defects in graphene on the adsorption characteristics of a single water layer and the electronic properties of the systems.

Following the previously reported structures\textsuperscript{47–49} where the electronic properties of each graphene unit cell is covered with water molecules forming six-membered rings with hydrogen bonding, we first construct the structure of a perfect periodic graphene surface about (17.0 ˚A $\times$ 14.8 ˚A) covered with a single water layer. Furthermore, based on the structure of perfect graphene, we construct structures of graphene with Stone–Wales and double vacancy (C$_2$) defects, the two commonly observed types of defect. Note that the structures of the two defects are represented as Stone–Wales (n) and C$_2$ vacancies (n), with n being the number of defects involved. Accordingly, we obtain three initial models of surfaces adsorbed with a single water layer. Fig. 1 shows the initial adsorption configuration with 32 water molecules. To address the effect of defect density on water adsorption, we respectively investigate graphene models constructed with 1–4 defects in each unit cell. To minimize the impact of the interaction between defects, the defects constructed in this work are separated by a complete six-ring. Considering the possibility of changes in the bonding characteristics, we do not freeze any carbon atoms in the graphene surface in the water adsorption dynamics simulations and structural optimization.

All molecular dynamics simulations are performed with a time step of 1 fs and a timescale of 50 ps. Each system is sampled more than three times to ensure that the results are reliable. By simulating the systems containing four defects at different temperatures (300 K, 200 K, and 100 K), we observe that the higher the temperature, the earlier the time (transition point) at which the dynamic system reaches equilibrium. A similar observation has been reported in ref. 21 (see more in the ESIF†). Therefore, we select a relatively stable structure based on the dynamics simulations after 20 ps at 300 K for further energy minimization. To better understand the impact of surface water and the types and density of the deficits on adsorption characteristics and electronic properties, we analyze the structural changes, the density of states, the charge density, the charge transfer, the molecular orbital characteristics, and other aspects and in addition make a comparison of the average adsorption energies.

Adsorption energy is calculated according to

$$E_{\text{ads}} = (E_{\text{gra+H$_2$O}} - E_{\text{gra}} - mE_{\text{H$_2$O}})/m,$$

where $E_{\text{ads}}$ is the adsorption energy per water molecule, $E_{\text{gra+H$_2$O}}$ the total energy of the system of graphene and water molecules at each step in the dynamics simulation output, $E_{\text{gra}}$ the total energy of a separately optimized graphene, $E_{\text{H$_2$O}}$ the total energy of a separately optimized water molecule, and $m$ the number of water molecules. In this way, adsorption energy is calculated for every step.

**Results and discussion**

The typical structures of the dynamics simulation at 300 K are shown in Fig. 2. The results indicate that in all systems, the single water layer cannot maintain the hydrogen bonding structure, reflecting a hydrophobic characteristic. Furthermore, the perfect graphene and the graphene with C$_2$ vacancy defects both show relatively good stability, without any obvious deformation in their structures. The graphene with Stone–Wales defects wrinkles obviously, removes the water molecules, and then relaxes its Stone–Wales defects. The wrinkles do not disappear entirely at the end, indicating that the graphene with a stable Stone–Wales defect is bent, The result is in good agreement with previous reports.\textsuperscript{52} For understanding better the structural characteristics of the different systems, we analyzed the IR vibrational spectra calculated using the same DFTB method, and we also identified the vibrational modes relating to Stone–Wales and C$_2$ vacancy defects (see Fig. S5 in the ESIF†).

To compare the time evolutions of the system features with different defect densities, we present a typical dynamics
simulation process at 300 K. Fig. 3(a) and (b) shows that, referenced to the perfect graphene, the C₂ vacancy defect system can reach equilibrium more easily than the obviously curved Stone–Wales defect system. We further calculate the average adsorption energy of the dynamics simulation between 30 ps and 50 ps and compare it with the adsorption energy of the optimized structure, as shown in Table 1. Due to the temperature effect of dynamics models, the average adsorption energy of a dynamics simulation is obviously less than that of the optimized structure (in brackets). The adsorption energy is \( \approx 5.29 \text{ kcal mol}^{-1} \) (\( \approx 10.58 \text{ kcal mol}^{-1} \)) for the water layer on perfect graphene, \( \approx 5.08 \text{ kcal mol}^{-1} \) (\( \approx 10.51 \text{ kcal mol}^{-1} \)) for the water layer on graphene with four C₂ vacancy defects, and \( \approx 5.14 \text{ kcal mol}^{-1} \) (\( \approx 10.60 \text{ kcal mol}^{-1} \)) for the water layer on graphene with four Stone–Wales defects. Thus, even at high defect densities, both the C₂ vacancy defects and the Stone–Wales defects only have a weak influence on the hydrophilic and hydrophobic properties of graphene, with negligible adsorption energy changes (less than 0.1 kcal mol\(^{-1}\)), indicating that graphene has a relatively stable hydrophobicity.

To understand the impact of C₂ vacancy defects and the Stone–Wales defects on the interaction of graphene and water, we further analyzed the density distributions of the oxygen (Fig. 4(a)) and hydrogen (Fig. 4(b)) atoms in water molecules along the direction perpendicular to the surface of the graphene (taking the average in the last 10 ps in the corresponding equilibrium stage of the simulation). We observed that the density distribution of oxygen atoms was relatively stable (the peak appears at approximately 3.3 Å from the graphenes), compared with the data in Table 1, showing little effect of defects on the oxygen density. Interestingly, the density distribution of the hydrogen atoms reflects H–π interactions of the water atoms and the graphene surface. Similar to that on the surface of a perfect graphene, the density distribution of hydrogen atoms on the surface with Stone–Wales and C₂ vacancy defects also show two peaks (at around 2.4 Å and 3.7 Å), qualitatively consistent with the double-peak feature of hydrogen density distribution in the previous reports of DFT-based dynamics simulation.\(^{50}\)

Unlike previously reported cases in which the –OH and –COOH functional groups could cause an adsorption enhancement for a small water cluster,\(^{15,23,24,29}\) Stone–Wales and C₂ vacancy defects are still dependent on the H–π interactions in binding the water molecules instead of on the stronger hydrogen bonding interactions, such as those in the cases of the –OH and –COOH functional groups, due to the fact that the two commonly observed defects do not damage the sp² hybridization characteristics of the C atoms in the graphene (as shown in Fig. 2).

Understanding the electronic properties of a single water layer adsorbed on graphene is important for guiding graphene’s applications. We further study the density of states (DOS), the charge density, the charge transfer, and the characteristics of the molecular orbits of the structures optimized after DFTB molecular dynamics simulations (see Fig. 5, S7 and S8 in ESI†). First, we analyze the possible effect of an adsorbed single water

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**Fig. 1** The initial configuration of a single water layer adsorbed on (a) smooth perfect graphene; (b) graphene with four double vacancy defects; and (c) graphene with four Stone–Wales defects.

**Fig. 2** The typical structures in the molecular dynamics simulations of a water layer adsorbed on (a) and (d) smooth perfect graphene; (b) and (e) graphene with a C₂ vacancy defect; and (c) and (f) graphene with Stone–Wales defects. Figures (a–c) are top views, and (d–f) are side views.
adsorbed water (dashed line), the peak values of the graphene adsorbed with water (solid line) are shifted to the lower energy side. In the ESI,† we provide similar DOS results for graphene with a different number of defects (1, 2, and 3) which show that their peaks have the same characteristics as the one here with four defects. As shown in Fig. 5, the DOS peak of water–graphene is mainly determined by the structural characteristics of graphene, presenting a negligible shift (about 0.1 eV) upon water adsorption and thus still embodying graphene’s good stability in terms of maintaining its electronic properties.

On the other hand, the adsorption of the single water layer obviously generates some new peaks. To understand further the origin of typical peaks in the case of water adsorption, we draw the orbitals corresponding to the peak position of the three kinds of water systems, as shown in Fig. S8.† Fig. S8(a)† shows the DOS result of perfect graphene with a peak value at −8.55 eV and an intensity of 9.05 eV⁻¹; Fig. S8(b)† presents the DOS result of graphene with four C₂ vacancy defects with a peak value at −8.57 eV and an intensity of 8.52 eV⁻¹; and Fig. S8(c)† gives the DOS result of graphene with four Stone–Wales defects with a peak value at −8.61 eV and an intensity of 10.32 eV⁻¹. As Fig. 5 and S7† show, these orbitals have the obvious dumbbell-shaped orbital characteristics of the p electrons. It can be seen that these peaks are mainly contributed by the p-orbital of O atoms and C atoms.

Based on Fig. 5 and S8,† we analyze the impacts of the single water layer on the band gap width. The results in Table 2 show that the band gap width becomes slightly narrowed to less than 0.01 eV when the single water layer is adsorbed on the surface of perfect graphene. Similarly, when the single water layer on the graphene contains Stone–Wales defects or C₂ vacancy defects, with changes in the number of defects, the band gap changes irregularly to a certain degree but only within 0.01 eV. Thus, graphene itself is a very stable material (i.e., the conductivity of graphene is mainly determined by the type and number of defects in its unit cell). From Table 2, we can see that regardless of whether there are water molecules or not, the presence of Stone–Wales defects or C₂ vacancy defects will make the band gap narrow to about 0.19–0.32 eV and 0.33–0.58 eV, which is obviously about an order of magnitude larger than the impact of the water. The band gap of the graphene with a single water layer (or without a single water layer) becomes about 0.01–0.33 eV (or 0.01–0.30 eV) narrower in the case with C₂ vacancy defects than it does in the case with Stone–Wales defects, indicating that the conductivity of the graphene with C₂ vacancy defects is stronger than that of the graphene with the Stone–Wales defects. In particular, the band gap of the graphene with four C₂ vacancy defects is the narrowest (0.39 eV versus 0.37 eV between the cases with no single water layer and with a single water layer on graphene) and shows the best conductivity.

Charge transfer is shown to occur when the single water layer is adsorbed on the surface of the graphene with the defective structures. However, for all of the types of defects in our study, the results such as those shown in Table 3 reveal that the charge transfer from the graphene to the 32 water molecules is just about 0.072 e. The order of magnitude of the results is consistent with that in the previous results based on DFT.†

Table 1 The average adsorption energy for the period from 30 ps to 50 ps in molecular dynamics simulations and the adsorption energy at 50 ps with further structural optimization for perfect graphene, graphene with four C₂ vacancy defects, and graphene with four Stone–Wales defects, respectively.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ads/E kcal mol⁻¹ (MD)</th>
<th>Ads/E kcal mol⁻¹ (Opt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene-H₂O</td>
<td>−5.29</td>
<td>−10.58</td>
</tr>
<tr>
<td>C₂ vacancy(4)-H₂O</td>
<td>−5.08</td>
<td>−10.51</td>
</tr>
<tr>
<td>Stone-Wales(4)-H₂O</td>
<td>−5.14</td>
<td>−10.60</td>
</tr>
</tbody>
</table>

Fig. 3 The comparison of the adsorption energies of the water–perfect graphene and water–graphene with defects at 300 K: (a) the case of water–C₂ vacancy defects and (b) the case of water–Stone–Wales defects. The green, purple, and pink lines represent the adsorption energies of the water–perfect graphene, the water–graphene with C₂ vacancy defects, and the water–graphene with Stone–Wales defects, respectively.

Fig. 4 The density ρ of O and H of water layers on graphenes with four defects of the Stone–Wales defects (purple line) and C₂ vacancy defects (green line), perfect graphene (blue line). (a) The ρ of O; and (b) the ρ of H.

Fig. 5 DOSs of graphenes with four defects of each of the two defect types and perfect graphene with (solid line) and without (dotted line) an adsorbed water layer. (a) Graphene with four Stone–Wales defects; (b) graphene with four C₂ vacancy defects; and (c) perfect graphene. The arrows indicate the positions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the vertical bar between them is the Fermi level, with black for graphene and red for graphene with the water layer.
Wales and C2 vacancy defects, the two most commonly observed defects that may affect graphene’s performance in practice. Our study clearly shows that the hydrophilic and hydrophobic properties of graphene remain unchanged even when it contains Stone–Wales and C2 vacancy defects, the two most commonly observed defects. This stable property is retained even with the adsorption of a single water layer. We hope that this research will promote applications of graphene in many areas, including biology and materials science.

**Conclusions**

In summary, the structural and electronic properties of a single water layer on perfect graphene, graphene with Stone–Wales defects, and graphene with C2 vacancy defects have been studied by performing quantum-mechanical level DFTB computations. Analysis of the structures and the adsorption energy of these systems reveals that the structure of graphene with Stone–Wales defects is obviously curved but the structures of perfect graphene and graphene with C2 vacancy defects are not. Stone–Wales defects or C2 vacancy defects can only adjust the hydrophilic and hydrophobic properties of graphene slightly, with the interaction strength varying within 0.1 kcal mol⁻¹. Hence, graphene has very good stability. Defects can adjust the charge transfer between the single water layer and the graphene in the various systems only on the magnitude of 0.01 e, showing little change compared with the system without defects (perfect graphene). The water adsorbed on the surface of graphene with the same density but different types of defects results in slight band gap changes within 0.01 eV, showing that the band gap of the system is primarily determined by the inherent characteristics of the graphene. The band gap of defective graphene is narrower than that of perfect graphene, showing possible tuning in the conductivity of graphene, with the effect of C2 vacancy defects being stronger than that of Stone–Wales defects. Therefore, the main characteristics of the systems of water adsorption on the three kinds of graphene surface are mainly affected by the type of defects in the graphene, which illustrates the good stability of graphene. Although it has high application potential in life sciences, materials science, and many other areas, graphene contains defects that may affect its performance in practice. Our study clearly shows that the hydrophilic and hydrophobic properties of graphene remain unchanged even when it contains Stone–Wales and C2 vacancy defects, the two most commonly observed defects. This stable property is retained even with the adsorption of a single water layer. We hope that this research will promote applications of graphene in many areas, including biology and materials science.

**Table 2** Band gaps of perfect graphene, graphene with C2 vacancy defects, and graphene with Stone–Wales defects adsorbed with a water layer. The n represents the number of defects, and the data in brackets indicate the band gaps of the systems with no water molecules adsorbed.

<table>
<thead>
<tr>
<th>Band gap/eV</th>
<th>n = 0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 vacancy(n)-H2O</td>
<td>0.96 (0.97)</td>
<td>0.52 (0.51)</td>
<td>0.61 (0.61)</td>
<td>0.63 (0.64)</td>
<td>0.37 (0.39)</td>
</tr>
<tr>
<td>Stone–Wales(n)-H2O</td>
<td>0.96 (0.97)</td>
<td>0.77 (0.77)</td>
<td>0.77 (0.78)</td>
<td>0.64 (0.65)</td>
<td>0.70 (0.69)</td>
</tr>
</tbody>
</table>

**Table 3** The charge transfer of the water layer adsorbed on the surface of perfect graphene, graphene with 4 C2 vacancy defects, and graphene with 4 Stone–Wales defects. The n represents the number of defects in the graphene.

<table>
<thead>
<tr>
<th>Charge transfer (e)</th>
<th>n = 0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 vacancy(n)-H2O</td>
<td>0.072</td>
<td>0.067</td>
<td>0.060</td>
<td>0.083</td>
<td>0.083</td>
</tr>
<tr>
<td>Stone–Wales(n)-H2O</td>
<td>0.072</td>
<td>0.077</td>
<td>0.080</td>
<td>0.090</td>
<td>0.061</td>
</tr>
</tbody>
</table>

Interestingly, the charge transfer is similar (within 0.01 e of deviation) when defects are present. Thus, it is once again proved that graphene that contains both kinds of commonly observed defects retains its stable electrical characteristics.

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**Notes and references**


